Ultrafast photochemistry of photosynthetic reaction centre mimics

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Produced on archival quality paper
Dedicated to my parents,
Christel and Charles Robotham.
Abstract

In this work the photoinduced electron transfer (ET) behaviour of several photosynthetic reaction centre (RC) mimics was investigated. Particular attention was given to the decay pathways following excitation of the porphyrin $S_2$ state. The systems studied are linked either by covalent or supramolecular means or a combination of both. The redox-active chromophores include zinc(II) tetraphenylporphyrin (ZnTPP), tin(IV) tetraphenylporphyrin (SnTPP), buckminsterfullerene ($C_{60}$), an amino-substituted naphthalene diimide (ANDI) and several N-substituted naphthalene diimides (NDIs). A boron dipyrromethene (BODIPY) is employed as an energy transfer (EnT) partner.

The time scales of the investigated processes required the use of ultrafast transient absorption (TA) measurements. The design and construction of the first implementation of a multichannel broadband detection TA instrument using a high repetition rate (94 kHz) amplified laser source is described. A hybrid global target analysis method, which allows TA data to be fitted by both sequential and branched decay scheme models, is also presented.

In non-covalently bound ZnTPP:$C_{60}$ complexes ET originating directly from the porphyrin $S_2$ state is observed. Rapid charge recombination partially reforms both the ZnTPP $S_1$ state as well as the ground state species. In a covalently linked ZnTPP-ANDI dyad a very similar behaviour is observed, although in this case charge recombination returns the ZnTPP $S_1$ state near quantitatively. In
both cases a non-thermalised charge separated state can be inferred. If a further thermalised charge separated state is energetically accessible from the porphyrin $S_1$ state, a second ET step to the same acceptor can occur. In supramolecular complexes of ZnTPP with either dipyridine naphthalene diimide (pyrNDI) or diisoquinoline naphthalene diimide (isoquinNDI), ET commencing from the former’s $S_1$ state to the NDI acceptors is observed. Isoquinoline coordination to the porphyrin metal centre, as it occurs in the ZnTPP:isoquinNDI complex, has not been previously reported as an assembly method for RC mimics. In this system the possibility of a very similar higher excited state behaviour as in the ZnTPP-ANDI dyad, i.e. ET from the porphyrin $S_2$ state followed by charge recombination to its $S_1$ state, is inferred. ET from the porphyrin $S_2$ state does not require a covalent link to the employed acceptor, although a small chromophore separation and the proximity of the frontier orbitals thereby ensured are a necessity.

Finally, the photophysics of an NDI$_2$-SnTPP:(OPh-BODIPY)$_2$ array and several related model systems was investigated. In the NDI$_2$-SnTPP:(OH)$_2$ triad, ET from SnTPP to an NDI moiety is exclusively observed for porphyrin $S_2$-excitation. The product of subsequent charge recombination, either the porphyrin $S_1$ state or the ground state species, is strongly dependent on the solvent polarity. In the arrays containing both SnTPP and BODIPY the former’s $S_2$ state can undergo EnT to the latter’s $S_1$ state. However, rapid ET from the interlocated phenolate linker moiety to SnTPP is the dominant quenching process of the $S_2$ state in these arrays.
Declaration

This is to certify that:

(i) the thesis comprises only my original work towards the PhD except where indicated in the Preface,

(ii) due acknowledgement has been made in the text to all other material used,

(iii) the thesis is fewer than 100,000 words in length, exclusive of tables, maps, bibliographies and appendices.

Benjamin Edward Robotham
June, 2013
The following conference presentations and journal publications have resulted from the work presented in this thesis:

**Publications**

- Photophysics of untethered ZnTPP-fullerene complexes in solution  
  *Journal of Physical Chemistry A*, 2011 115 (44), 12217-12227

- Ultrafast electron transfer in a porphyrin-amino naphthalene diimide dyad  
  B. Robotham, K.A. Lastman, S.J. Langford and K.P. Ghiggino  
  *Journal of Photochemistry and Photobiology A*, 2013, 251, 167-174

**Conference presentations**

- Poster entitled 'Time-resolved spectroscopy of photosynthetic mimics'  
  *The Australasian Conference on Optics, Lasers and Spectroscopy, Adelaide, Australia*  
  November 2009

- Poster entitled 'Ultrafast spectroscopy of photosynthetic mimics'  
  *6th Asian Photochemistry Conference, Wellington, New Zealand*  
  November 2010

- Poster entitled 'Ultrafast spectroscopy of electron transfer in porphyrin donor dyads'  
  *7th Asian Photochemistry Conference, Osaka, Japan*  
  November 2012
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List of abbreviations

ANDI  Amino-substituted Naphthalene Diimide ........................................ 31

BODIPY  Boron Dipyrromethene ......................................................... 4

C$\text{_{60}}$  Buckminsterfullerene .......................................................... 4

CA  Coherent Artefact .............................................................................. 55

CR  Charge Recombination ......................................................................... 10

CS  Charge Separated (Charge Separation) .................................................. 1

DADS  Decay-Associated Difference Spectra ............................................... 82

DCM  Dichloromethane .............................................................................. 19

DFT  Density Functional Theory ............................................................... 25

EADS  Evolution-Associated Difference Spectra ......................................... 82

EFA  Evolving Factor Analysis .................................................................. 80

ET  Electron Transfer ................................................................................ 1

EnT  Energy Transfer ................................................................................ 3

EPR  Electron Paramagnetic Resonance ...................................................... 25
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<td>Group Delay Dispersion</td>
</tr>
<tr>
<td>GLA</td>
<td>Global Lifetime Analysis</td>
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<tr>
<td>GTA</td>
<td>Global Target Analysis</td>
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<tr>
<td>HOMO</td>
<td>Highest Occupied Molecular Orbital</td>
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<tr>
<td>IC</td>
<td>Internal Conversion</td>
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<tr>
<td>IRF</td>
<td>Instrumental Response Function</td>
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<tr>
<td>ISC</td>
<td>Inter-System Crossing</td>
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<td>isoquinMOD</td>
<td>N-(5-isoquinolinyl)-acetamide</td>
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<td>isoquinNDI</td>
<td>Diisoquinoline Naphthalene Diimide</td>
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<tr>
<td>LHC</td>
<td>Light Harvesting Complex</td>
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<td>LOF</td>
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<td>NMR</td>
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<td>ODE</td>
<td>Ordinary Differential Equation</td>
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<td>OPA</td>
<td>Optical Parametric Amplifier</td>
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<td>Diquinoline Naphthalene Diimide</td>
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<td>RC</td>
<td>Reaction Centre</td>
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<td>RR</td>
<td>Repetition Rate</td>
</tr>
<tr>
<td>SADS</td>
<td>Species-Associated Difference Spectra</td>
</tr>
<tr>
<td>SAS</td>
<td>Species-Associated Spectra</td>
</tr>
<tr>
<td>SAXS/WAXS</td>
<td>Small- And Wide-Angle X-ray Scattering</td>
</tr>
<tr>
<td>SCE</td>
<td>Saturated Calomel Electrode</td>
</tr>
<tr>
<td>SHG</td>
<td>Second Harmonic Generation</td>
</tr>
<tr>
<td>SLM</td>
<td>Spatial Light Modulator</td>
</tr>
<tr>
<td>S/N</td>
<td>Signal-To-Noise Ratio</td>
</tr>
<tr>
<td>SnTPP</td>
<td>Tin(IV) Tetraphenylporphyrin</td>
</tr>
<tr>
<td>SVD</td>
<td>Singular Value Decomposition</td>
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<tr>
<td>TA</td>
<td>Transient Absorption</td>
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List of abbreviations

**TCSPC** Time-Correlated Single Photon Counting ........................................ 22

\( \Delta t_0 \) Time Zero .................................................................................. 59

**TTL** Transistor-Transistor Logic ................................................................. 68

**WLC** White Light Continuum ........................................................................ 58

**ZnTPP** Zinc(II) Tetraphenylporphyrin ......................................................... 19

List of non-SI base units

\( \checkmark \) Ångström \((10^{-10} \text{ m})\) ......................................................... 27

eV electronvolt ................................................................................................. 141

fs femtosecond ............................................................................................... 23

kHz kilohertz .................................................................................................... 55

M molar \((\text{mol/dm}^3)\) ..................................................................................... 110

MHz megahertz ................................................................................................. 54

\( \mu \) g microgram .......................................................................................... 51

\( \mu \) M micromolar \((10^{-6} \text{ mol/dm}^3)\) ......................................................... 52

\( \mu \) s microsecond ........................................................................................ 24

mm millimetre .................................................................................................... 52

mM millimolar \((10^{-3} \text{ mol/dm}^3)\) ................................................................. 111
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<th>Abbreviation</th>
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<tr>
<td>mOD</td>
<td>optical density ( \times 10^{-3} )</td>
<td>59</td>
</tr>
<tr>
<td>ms</td>
<td>millisecond</td>
<td>24</td>
</tr>
<tr>
<td>mW</td>
<td>milliwatt</td>
<td>54</td>
</tr>
<tr>
<td>nm</td>
<td>nanometre</td>
<td>53</td>
</tr>
<tr>
<td>nJ</td>
<td>nanojoule</td>
<td>63</td>
</tr>
<tr>
<td>ns</td>
<td>nanosecond</td>
<td>22</td>
</tr>
<tr>
<td>ps</td>
<td>picosecond</td>
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Chapter 1

Introduction

1.1 Background

In photosynthetic systems photon derived excitation energy is funneled towards the reaction centre (RC) where it is rapidly converted into a long-lived charge separated (CS) state via several sequential electron transfer (ET) events. The oxidised donor and the reduced acceptor then drive further redox reactions. In nature this involves the oxidation of water and the reduction of CO$_2$ to form O$_2$ and organic compounds. Effectively photon energy is converted and stored in the form of chemical energy. Successfully mimicking this process in artificial systems would allow the utilising and storing of solar energy [1–9].

Currently natural photosynthesis is used to store solar energy in the form of high energy compounds which then can be processed to what is referred to as biofuels, e.g. from crop plants or algae. All of the energy currently consumed in the form of fossil fuels was originally captured by photosynthesis. Due to the problems arising from the use of fossil fuels, both the interest and implementation of biofuels have grown rapidly in previous years. However, as during the evolution of photosynthetic organisms usually factors other than light have been the limiting resource, e.g. water or nutrients, natural photosynthesis is not very efficient in net energy conversion.
terms and typically only a few percent of the incident radiation energy are stored within high energy compounds [1, 6–8, 10–12].

The advantages of photosynthetic fuels are high energy density, ease of transport and a highly developed infrastructure and technology for processing, e.g. refineries, pipelines and filling stations. The problem in trying to replace fossil fuels with biofuels arises when demand and low conversion efficiencies for biofuel production require vast areas of agricultural land to be set aside. Considering the problem of sufficient food production for a growing global population this obviously has considerable limitations.

An alternative is to convert solar energy into electricity via photovoltaics or concentrated solar thermal plants, but as electricity storage still lags behind chemical fuels in terms of both cost and energy density despite extensive research and development, this approach is currently also limited with regard to implementation on a large scale.

1.2 Artificial photosynthesis

The ideal solar energy conversion technology captures photons across the entire solar wavelength range, stores this energy within the chemical bonds of a high energy compound synthesised from a low energy compound feedstock and is made of abundant and environmentally friendly materials [8]. Based on this several different approaches are currently being pursued with varying success with regard to these requirements [10]. Considering that natural photosynthesis has a very high quantum efficiency and is recently also reasonably well understood [2, 4, 13–15], nearly all artificial approaches take inspiration from it.

One intensely researched area is photocatalytically splitting water into H₂ and O₂,
the former being the high energy compound (or a precursor to it) that could be transported and then recombined with oxygen to release the stored energy [3, 5, 6, 8, 12].

While considerable progress has been made towards developing systems capable of this using a variety of molecular or semiconductor materials, the issues of stability, material availability and cost are still limiting an economically viable implementation [8, 10, 12].

As the understanding of the components and processes in the natural system have greatly advanced within recent years, especially with regard to energy transfer (EnT) within the light harvesting complex (LHC), ET within the RC and other protein systems and the redox catalysis at the water splitting site [2, 8, 13–16], many current approaches try to mimic this at the molecular scale. This ranges from a focus on individual components such as the LHC or RC to the combination of these with nano-particles, semiconductors, vesicles or natural enzymes [7, 8, 11, 12, 17].

The overall success of this field requires a better understanding of how to build artificial LHCs and RCs and how to link these with a redox catalyst. Complex synthesis and the use of non-abundant materials inevitably cannot be part of a viable system. The complexity of the natural system, which combines a vast number of molecules structurally and energetically finely tuned, indicates that this is a difficult task [1, 3, 5, 6, 8–10].

The fundamental quantum mechanical mechanisms of light absorption, internal conversion (IC), electron transfer (ET), EnT and redox catalysis are shared between all natural and artificial approaches regarding solar energy conversion. Therefore mechanistic insights gained from a given research avenue are likely to be useful in the understanding of another.
1.3 Artificial reaction centres

1.3.1 Employed chromophores

The choice of employed chromophores is a combination of inspiration from the natural system’s chromophores (e.g. chlorophylls, quinones, carotenoids), redox suitability as a donor or acceptor for photoinduced ET, chemical stability and synthetic accessibility. In many systems both the reaction centre and light harvesting are mimicked by EnT between chromophores preceding the ET events that yield a charge separated state.

Due to their similarity to chlorophylls and numerous extensive studies on properties and synthesis a wide range of both freebase and metal porphyrins have been employed in artificial RC mimics, typically as the electron donor [3, 17–61]. Phthalocyanines [21, 30, 40, 45, 62–67], chlorophylls [68] and chlorins [69, 70] have been employed in a similar fashion. Other electron donor chromophores have been triphenyl diamine [71], carotenoids [7, 64], boron dipyrrromethene (BODIPY) [72] and dimethyl julolidine [73, 74]. In systems containing more than two chromophores some of these can act as both electron acceptor and donor, as the character particular to the system depends on the relative ordering of the redox potentials. Examples of this are porphyrins [7, 42] and anthracene [58, 73, 75].

Due to its redox properties and low reorganisation energy buckminsterfullerene (C\textsubscript{60}) has been a very frequently employed electron acceptor [18, 22, 24–31, 34, 39, 46, 48, 50, 57–59, 66, 67, 72, 76]. Other electron acceptors include benzoquinone [41, 45, 53, 65] and the related tetracyanonaphthoquinidodimethane [41].

An increasingly expanding group of employed chromophores are aromatic imides such naphthalene diimides (NDIs) [20, 23, 28, 30, 32, 35, 36, 49, 54, 60–62, 68, 73,
1.3. Artificial reaction centres

74, 77–80] and perylene diimides (PDIs) [38, 47, 51, 55, 63, 68, 71, 76, 80–82]. Their benefits lie in good chemical stability, redox suitability and synthetic ease of tuning properties such as redox potentials, excitation energies and solubility. Whereas the imide substituents have little impact on the energetics of the chromophore, attaching electron donating or withdrawing side groups to the aromatic core can considerably change its characteristics, for example redox potentials, excitation energies and fluorescence yield [23, 69, 70, 83–87]. Solubility can be tuned by using bulky side groups as either core or imide substituents to prevent aggregation [23, 47, 86].

Transition metal complexes, especially ruthenium based, are commonly used in dye sensitised solar cells to transfer electrons into TiO$_2$ nanoparticles and are investigated as redox catalysts for water splitting. Some ruthenium complexes and ferrocene have been employed in RC mimics [7, 12, 17, 46, 76, 79, 87–89]. Low-lying energy levels arising from the metal d-orbitals allow for additional deactivation pathways of excited states and thereby introduce undesired competition for the formation of a CS state via ET. This and the necessity of having to use abundant materials for a working system complicate their applicability [1, 11, 12].

1.3.2 Covalent architectures

Whereas the chromophores of the natural system are held in place by a protein matrix, a simpler approach is to tether the chosen chromophores with a covalent linker. Within the limits of synthesis there is a choice of where the linker attaches to the chromophore, its length, its flexibility or rigidity, chemical composition, $\sigma$-to $\pi$-bond ratio, its energetics relative to the chromophores and how many linkers connect how many chromophores. All this amounts to a vast variable space with an essentially endless number of possible systems [1, 8].

The simplest class of systems in terms of both synthesis and analysis are so-called
dyads, which have been investigated extensively [18–20, 26, 29, 34, 38, 52, 53, 56, 59, 63, 65, 66, 69, 72, 75, 81, 90, 91]. Larger systems become synthetically more challenging, but there have been numerous investigations into triads [11, 63, 69, 88, 91], tetrads [34, 42], pentads [62] and larger systems up to heptads [58]. These are systems with at least some degree of redox gradient amongst different chromophores. Single covalent molecules containing a higher number of chromophores have been synthesised, but in these cases they usually involve multiple identical chromophores linked either to a dendrimer [1, 32, 80] or an oligomer backbone [78, 84, 85].

Rigid linkers minimise the conformational freedom and thereby fix the parameters of distance and orientation between chromophores. Although this is usually synthetically more challenging, it allows easier access to some of the ET parameters [41, 65, 73, 75, 89, 92]. Flexible linkers are synthetically easier to achieve, which is an advantage with respect to creating a useful system, but obviously allow a range of conformations and distances between the chromophores, which are hard to determine experimentally and might not necessarily improve the system’s function [9, 22, 27, 29, 47, 57, 71, 81, 92]. Apart from determining the distance and orientation of the chromophores the linker can also affect the electronic coupling. As
1.3 Artificial reaction centres

this depends partially on the energetics of the bridge orbitals compared to those of the chromophores, the effect of \(\pi\)-bonds and aromatic components within the linker has also been investigated [41, 65, 73, 74, 89, 92].

1.3.3 Supramolecular architectures

Considering that not only the molecules making up the RC need to be linked, but the RC, the LHC and the redox active centre with each other, it is clear that a fully covalent system is not feasible [9]. This insight, combined with the inspiration from the natural system and the growth of the field of supramolecular chemistry, has led to an increasing number of RC mimics in which the chromophores are not linked covalently. These range from dyads [30, 35, 36, 61] to larger systems in which some chromophores are linked covalently and others in a supramolecular fashion [28, 30, 46, 48, 55, 70, 79, 80, 93].

The following binding motifs have been used:

- **Ligand to metal binding**
  
  This is frequently used for axial coordination to the metal centre of porphyrins and related compounds. Examples are N-donors to Zn [28, 30, 36, 55, 58, 70, 94] or Ru [46, 79] and O-donors to Al, Si or Sn [30, 37, 79].

  ![Figure 1.2: Typical example of a ligand to metal coordination link [36].](image)

- **Hydrogen bonding**
  
  This binding motif is ubiquitous in biological systems and in principle allows
highly selective and strong binding when several hydrogen bonds are placed in parallel. The use of hydrogen bonds in RC mimics ranges from using one or more to arrange chromophores in a covalently linked system \[46, 53, 70\] to being the only tethering between chromophores. Examples of the latter are the complimentary binding of amidinium to a carboxylate or sulfonate group via two hydrogen bonds \[61\] or similarly the binding of triaminotriazine to the end of a H-terminated NDI via three hydrogen bonds \[35\].

Figure 1.3: Typical example of a hydrogen-bond link \[35\].

- \(\pi-\pi\) interactions

As many of the employed chromophores are aromatic, e.g. NDIs and PDIs, the resultant \(\pi-\pi\) attractions lend themselves to arranging such molecules in ordered face to face arrangements. One advantage of this binding motif is that it is possible to arrange a large number of chromophores in an ordered stack, another is that the relative distances and orientations are much more controlled \[9, 69, 80, 85, 95\].

Figure 1.4: Typical example of \(\pi-\pi\)-stacked assembly of NDIs \[85\].
1.3. Artificial reaction centres

- **Ionic interactions**

Whereas ligand to metal complex binding is used predominantly as a structural tool, the coordination of free metal ions such as Mg\(^{2+}\) or Sc\(^{3+}\) to either the ground state, the radical anion of the CS state or both can affect the energetics of the system, allowing these to be tuned to some extent [23, 24, 26, 42, 48, 52, 54, 63, 96].

![Ionic binding motif](image)

Figure 1.5: Typical example of an ionic binding motif involving a metal ion [96].

The issues arising from the conformational flexibility of some supramolecular linkers are similar to those described above for covalent connections [85]. An additional problem is the possibility of reversible binding, which is usually suppressed by choosing links with high binding constants [30, 36]. This can also be achieved by using multiple supramolecular bonds or in combination with covalent connections, which will result in a binding greater than the sum of the individual links due to the chelate effect [53, 78, 84].

The greater scale of systems accessible with supramolecular architecture also opens up the possibility of emergent behaviour, i.e. properties that are not inherent to the individual chromophores [80]. This idea is supported by observations of quantum mechanical effects in the LHC of green sulfur bacteria, which contains twenty one bacteriochlorophyll molecules and appears to act as a single unit rather than as a mere collection of individual chromophores [13].
1. Introduction

1.4 Photoinduced electron transfer

ET is an elementary process of chemistry and ubiquitously found in the natural world. In photosynthesis, following initial excitation and EnT within and then from the LHC to the RC, several ET steps result in a CS state, in which the negative electron and the positive hole resulting from an unbalanced nuclear charge are spatially separated. This represents an electric and redox potential and the energy contained within is then utilised to drive further endothermic chemical reactions.

In artificial photosynthetic RC mimics the desired outcome is ET from the initial donor to the final acceptor leading to a CS state sufficiently long-lived that this redox potential can be passed on to the redox catalytic site. This process has to compete with other decay pathways of the initial excited state, e.g. EnT, photoluminescence and IC as well as avoiding charge recombination (CR). In a system combining a RC and a redox catalyst the electron would be passed on to the latter and thereby shorten the CS state’s lifetime. The lifetime of the CS state is therefore not an end in itself. However, as the CS state lifetime in an isolated RC mimic gives a measure of the ratio of CS and CR rates, it should be as long as possible. A further goal is a high energy content of the CS state, therefore maximising the conversion of the absorbed photon’s energy to available redox potential.

The creation of a functioning artificial system requires understanding and constructively implementing the complexities of ET. RC mimics have been used extensively to develop and test ET theory. The main basis of this is Marcus theory, developed by Rudolph A. Marcus, for which he received the Nobel Prize in chemistry in 1992 [97–99].
1.4. Photoinduced electron transfer

1.4.1 Marcus theory

During ET the entire system, this being donor, acceptor and medium, has to distort so that the initial state and the final CS state are degenerate. The thermal activation barrier to this is given by:

$$\Delta G^\# = \frac{(\Delta G + \lambda)^2}{4\lambda}$$  \hfill (1.1)

where $\Delta G^\#$ is the activation energy, $\Delta G$ the free energy difference between the initial and final equilibrium states and $\lambda$ the reorganisation energy necessary to deform the reactant to the product geometry. When the inter-system crossing (ISC) point between the two states is reached via thermal activation, electron tunnelling occurs. In the weak coupling limit of non-adiabatic ET the probability is proportional to the square of the electronic coupling $V_{DA}$ between the initial and final states. Under these conditions the rate of ET is

$$k_{ET} = \frac{2\pi^{3/2}V_{DA}^2 e^{2\Delta G^\# / k_B T}}{h(\lambda k_B T)^{1/2}}$$  \hfill (1.2)

where $h$ is the Planck constant and $k_B$ Boltzmann’s constant. The rate reaches its maximum when the driving force equals the reorganisation energy and the activation energy hence becomes zero [16, 30, 38, 41, 45, 63, 68, 100].

Driving force

The Rehm-Weller equation can be used to estimate the driving force [101]:

$$\Delta G = e \times [E_{Ox}(D) - E_{Red}(A)] - E_{00} - \frac{e^2}{4\pi\epsilon_0 \epsilon_S R_{cc}}$$  \hfill (1.3)

where $e$ is the electron charge, $E_{Ox}(D)$ the first oxidation potential of the donor, $E_{Red}(A)$ the first reduction potential of the acceptor, $E_{00}$ the energy of the excited state, $\epsilon_0$ the vacuum permittivity, $\epsilon_S$ the solvent’s dielectric constant and $R_{cc}$ the centre to centre separation of the chromophores [41, 42, 101, 102]. This equation
is helpful in explaining observed solvent dependencies with regard to ET rates and lifetimes of the CS state [41, 42, 49, 52, 58]. However, the calculation of accurate values is limited, as the solvent does not represent a dielectric continuum at the molecular level. The actual solvent response is better understood as a combination of inertial and diffusional motion, with the latter depending on the solvent viscosity. At low magnitudes of $V_{DA}$ this effect is not relevant, while at higher values and increasing viscosity it can become the dominating limitation to the ET rate [82, 103].

Equally, the assumption of the two chromophores of the CS state to be point charges separated by $R_{cc}$ reaches its limitations at close proximities and charge delocalisation as often is the case in extended aromatic systems of the chromophores mentioned above. A certain improvement can be achieved by correction terms that account for the finite size of the chromophores by introducing ionic radii, but this will again start to deviate for non-spherical chromophores [41, 49, 102]. The overall accuracy is obviously related to the accuracy of the input variables. For example, $R_{cc}$ is hard to determine in the case of flexible linking and does not account for different chromophore orientations.

**Reorganisation energy**

The reorganisation energy $\lambda$ is typically broken up into an inner term $\lambda_i$, which deals with the chromophores' structural changes during ET, and an outer term $\lambda_s$, which deals with the reorientation of the surrounding solvent molecules. $\lambda_i$ is usually insensitive to the solvent polarity and can be derived from electronic structure calculations [73]. $\lambda_s$ is harder to determine in such a fashion as a considerable number of solvent molecules would need to be included in such a calculation. Similarly to the assumptions of the Rehm-Weller equation (1.3), it can be estimated by the following equation, in which $r_D$ and $r_A$ are the ionic radii of the donor and the
acceptor respectively and $n$ is the refractive index:

$$
\lambda_s = \frac{1}{4\pi \varepsilon_0} \left[ \frac{1}{2r_D} + \frac{1}{2r_A} + \frac{1}{R_{cc}} \right] \left[ \frac{1}{n^2} - \frac{1}{\varepsilon_s} \right]
$$

(1.4)

As polar solvent molecules will be more sensitive to a change in charge distribution, $\lambda_s$ increases with solvent polarity. The overall effect on the activation energy and hence rates and CS state lifetime depends on how the total reorganisation energy and the driving force balance [41, 42, 49, 52, 58, 73, 100].

**Electronic coupling**

The square of the electronic coupling matrix element $V_{DA}$ is a quantification of the probability of the electron tunnelling through the potential energy barrier separating donor and acceptor. As the barrier height is dependent on the chromophore separation, $V_{DA}$ quantifies the distance and orientation dependence of the ET rate. It is known that the coupling decreases exponentially with donor-acceptor separation. This can be explained qualitatively by decreasing orbital overlap [16, 39, 45, 53, 92, 104, 105]. As the orientation dependence cannot be described by a single coordinate (the description of the orientation of two chromophores relative to each other requires a minimum of four variables), a universally applicable mathematical description is hard to formulate and in practice requires electronic structure calculations [106]. In calculations of the coupling between two iron porphyrins it has been shown that it can vary up to two orders of magnitude at comparable centre to centre distances [107].

When structural parameters within the chromophores need to be considered, e.g. dihedral angles or the deviation from planarity in aromatic systems, an accurate estimation of $V_{DA}$ becomes complex [68]. As can be seen from (1.2), the ET rate depends weakly on $\lambda$ and temperature and strongly on the electronic coupling. However, this is only applicable within the weak coupling limit with $V_{DA} < k_B T$, as beyond this
rates faster than the vibrational modes that move the system along the reaction coordinate would be predicted [100].

**Inverted region**

From (1.1) it follows that as the driving force increases and becomes larger than the reorganisation energy, the activation energy starts to rise and the rate of ET accordingly to fall. This is referred to as the Marcus inverted region [98]. In most studied RC mimics the higher rate of forward ET leading to the CS state compared to the backward charge recombination ET step is explained by the CS step lying in the Marcus normal region and the CR, usually involving a larger free energy gap than the former, lying in the Marcus inverted region [30, 31, 38, 41, 52, 57, 84]. The higher driving force for CR can be qualitatively understood by the coulombic attraction of the hole and electron charges.

Experimentally this effect has been confirmed, although the decrease in rate with increasing driving force is less than predicted by (1.1) and (1.2) and CR appears to be barrierless ($\Delta G^\# = 0$) in the inverted region. This is attributed to quantum-mechanical tunnelling rather than thermal activation as being the dominant process of going from the reactant to product state [45, 100], although some debate remains [108]. It is therefore better described as a non-radiative transition from one electronic state to another [82]. The rate $k_{ET}$ can therefore by described by invoking Fermi’s Golden Rule:

$$k_{ET} = \frac{2\pi}{\hbar} V_{DA}^2 FCWD$$

(1.5)

where $FCWD$ is the Franck-Condon weighted density of states [82, 99]. An important consequence of (1.5) is that little to no temperature dependence on the ET rate is observed in the inverted region [45, 49, 73, 100].
1.4.2 Effect of linking moiety

The overall electronic coupling and the resulting rate of ET depend on the nature of the linking moiety between donor and acceptor and the available pathways thereby. The interaction might be via covalent or supramolecular linkers or through space. Depending on the system, either one of these processes dominates or otherwise dynamic averaging occurs [16]. Amongst the main factors affecting this are the structural and energetic properties of the linking moiety.

The first distinction is whether the latter merely mediates ET from the donor to the acceptor or whether it acts as an intermediate acceptor with the electron spending a finite time within. The latter is referred to as a hopping mechanism. Whether the linker can temporarily accept the electron depends on the energetics of its frontier orbitals compared to the donor and the acceptor. In systems containing saturated $\sigma$-bond linkers with energetically far removed frontier orbitals the electron passes from donor to acceptor in a so-called superexchange. Other systems which intuitively would rather be described as triads, tetrads, etc. display hopping [9, 16, 22, 29, 41, 51, 57, 58, 71, 73, 84, 100, 105]. Intermediate types include $\pi$-bonds or aromatic components within the linker. It is difficult to attribute increased ET rates to either an increase in $V_{DA}$ via so-called through bond coupling, resulting from the mixing of energetically proximate donor, bridge and acceptor orbitals, or alternatively electron hopping. The net effect of a stronger coupling of donor and acceptor by these types of linkers is however clearly observable [65, 73, 89, 92].

Structural flexibility of the linker introduces ambiguity into the experimental analysis as the confirmations are both hard to determine and most likely present as a distribution. It is known that orientational fluctuation slows ET rates [45] and flexible linkers enable conformational gating, in which some conformations either
1. Introduction

suppress or facilitate ET [92]. Bulk solution measurements yield an ensemble aver-
age and make this hard to discern [16, 80]. As the mixing of orbitals also depends on relative orientations, electronic structure calculations face similar problems [109].

1.4.3 Spin selectivity

When the CS state results from ET from the $S_1$ excited state, it has the same multiplicity, $^1$CS. ISC allows population of the triplet CS state, which of course might also be formed by direct ET from the $T_1$ excited state if energetically feasible. As the return to the singlet ground state is both formally spin forbidden and the electronic coupling between states of different spin multiplicity tends to zero, the lifetime of the $^3$CS state can be considerably longer than that of the $^1$CS state, if all of the excited triplet states of donor and acceptor are higher in energy, which depends on the investigated system. Such a picture has been attributed to several cases of atypically long-lived CS states [22, 49, 68, 104].

Figure 1.6: Spin specific deactivation pathways of the CS state; adapted from [100].

To avoid equilibration of the $^3$CS and $^1$CS states, which depletes the former due to the spin allowed CR from the latter, the energetic splitting of the two, double the value of the so-called exchange interaction $J$, has to have an increased magni-
1.4. Photoinduced electron transfer

As $|J|$ is assumed to be proportional to $V_{DA}^2$, this requires strongly coupled systems, which is contrary to the usual approach of weakly coupled chromophores and can be achieved by using very short linkers [9, 100]. There has been an ongoing discussion about the involvement of triplet CS and excited states in such systems [5, 100, 110–112], which currently remains unresolved.

This approach is appealing due to the prospect of simple systems with long CS lifetimes. But the risk of forming highly oxidising singlet oxygen from triplet oxygen, for which natural photosynthesis has evolved several defence mechanisms, has to be considered in the design of a functioning artificial system [3].

1.4.4 Exciplex formation

Many currently investigated supramolecular systems use $\pi-\pi$ interactions as a binding motif and other systems are structurally capable of bringing chromophores into a face-to-face arrangement. In this case an exciplex may rapidly form. Given suitable redox energetics the following ET is nearly barrierless as a consequence, which also leads to an independence of the ET rate on temperature [9, 29, 39, 45, 100, 113]. The increase in electronic coupling might not necessarily be evident from steady-state absorption spectra [71].

1.4.5 Ion binding

Similar to the use of supramolecular binding motifs as structural tools, the binding of small inorganic ions to chromophores has been investigated as a tool to modify the energetics of RC mimics. This has included $\text{Na}^+$, $\text{K}^+$, $\text{Mg}^{2+}$, $\text{Zn}^{2+}$, $\text{Pb}^{2+}$, $\text{Sc}^{3+}$ and $\text{Lu}^{3+}$ [42, 52, 54, 63, 96] as well as $\text{F}^-$ and $\text{Cl}^-$ [23, 26, 42]. Depending on the system and solvent employed, the binding can either already occur prior to excitation and affect both CS and CR or, in the case of some of the cations, be
selective towards the radical anion of the \textit{CS} state and only affect \textit{CR}. The presence of the ion affects both the redox potentials of the chromophores before and after \textit{CS} as well as the reorganisation energies, which in turn modify the rates of \textit{ET} and hence the \textit{CS} lifetime. By lowering the energy of the \textit{CS} state relative to that of the initial excited state, ion binding might also make otherwise thermodynamically prevented \textit{CS} possible \cite{42, 52, 96}.

1.4.6 Proton coupled electron transfer

In biological systems \textit{ET} is frequently coupled to near simultaneous proton transfer \cite{11}. The transmembrane proton gradient produced in natural photosynthesis is the energy reservoir for the following endothermic chemical reactions, and artificial mimics of this have been explored \cite{7, 8, 85, 91}. Although the initial \textit{ET} processes in the natural \textit{RC} itself are not proton coupled, the proximate water oxidation reactions partially are so \cite{114}. Model systems for proton coupled \textit{ET} studies are very similar to \textit{RC} mimic systems and have been investigated in a similar fashion \cite{11, 61, 88}.

1.4.7 Involvement of higher excited states

In the study of \textit{RC} mimics it is often assumed that if the initial electron donor is excited to an electronic state beyond that of the \textit{S}_1 state, for example the \textit{S}_2 state or higher, it will obey Kasha’s rule and rapidly relax via \textit{IC} to \textit{S}_1 before proceeding on any further pathways. This implies that the fraction of the incident photon’s energy, corresponding to the energy gap between the \textit{S}_1 and the initially populated excited state, is lost and not available for further redox reactions. Overcoming this is one of the motivations for studying the decay pathways of higher excited states.

There are well-known exceptions to Kasha’s rule such as azulene \cite{115} and tetramethylindanethione \cite{116}, which fluoresce appreciatively from their second excited
1.4. Photoinduced electron transfer

singlet state. The $S_2$ state of carotenoids is involved in the light harvesting of the natural photosynthetic system [117, 118]. Experimental improvements within the last decade have made it possible to study the propensity of the $S_2$ state to act as the immediate electron donor in a number of systems. In an early study employing azulene, benzazulene and xanthione as donors it was shown that this process does indeed occur. The formed CS state decays via CR to the $S_1$ state [119]. Concurrently zinc(II) tetraphenylporphyrin (ZnTPP) emerged as a very popular donor studied for this purpose.

The $S_2$ state of ZnTPP is a further exception to Kasha’s rule. Depending on the solvent it has a lifetime of $1 - 2.5$ picoseconds(ps) before relaxing to the $S_1$ state via IC with near unity. The quantum yield of fluorescence from return to $S_0$ is in the order of 0.1% [120, 121]. The slow IC is due to the large energy gap between $S_1$ and $S_2$ and the small horizontal displacement between their respective potential energy surfaces [122].

ET from the $S_2$ state of ZnTPP and related compounds has been observed in a number of systems. The acceptors employed have included loosely complexed dichloromethane (DCM) [123], acetophenone [124], 1,2,4-trimethoxybenzene [124] and iodide [125] as well as covalently bound imide chromophores [113, 126]. In all of these cases ET from $S_2$ is followed by CR to the $S_1$ state, which subsequently decays unaffected by the present quencher, as further ET is at this point energetically not feasible. A consequence of CR to $S_1$ rather than $S_0$ is that due to the thus reduced driving force this ET step is moved from the inverted towards the barrierless region and hence accelerated, and the CS lifetime accordingly reduced [124].

In the system of loosely complexed sulfonated ZnTPP and methylviologen ET can occur from both $S_2$ and $S_1$ before direct CR back to $S_0$. From the observation
of vibrationally excited ground states following CS from either $S_2$ or $S_1$ and subsequent CR and further considerations, electronic excitation of the CS state was inferred, although the possibility of vibrational excitation was not excluded [56]. In the study of a pyromellitic diimide axially ligated to ZnTPP a similar conclusion was drawn. Here the possibility of a “hot CS state” as the initial product of ET from $S_2$ was also suggested, although experimentally not observed [127].

In the study of a covalently linked Zn(II)porphyrin-naphthaleneimide dyad it was found that while ET from $S_2$ was followed by CR to $S_1$ similar to the cases described above, the thermally relaxed CS state lies below $S_1$ and allows for a second CS step to occur from the latter [60]. The initial CS state preceding $S_1$ formation is interpreted as being vibrationally excited. Vibrational relaxation to the thermally relaxed CS is concluded as at least partially competing with $S_1$ formation. This study claims to show the “first direct spectroscopic evidence for hot charge recombination to $S_1$ after $S_2$ excitation in porphyrin-acceptor systems”.

In the majority of the above mentioned studies into the decay processes of $S_2$ excited porphyrin-acceptor systems, the information is deduced from the fluorescence decay of $S_2$ and rise of $S_1$. Spectroscopic evidence of the other intermediates has only emerged recently and is a matter of ongoing investigation and discussion [60, 122, 127, 128].

Beyond the occurrence of ET from the porphyrin $S_2$ state in small donor-acceptor systems, it has also recently been observed at the interface of porphyrin derivatives with the n-type semiconductor and common organic solar cell component indium tin oxide [33]. While slightly removed from the focus of this work, it demonstrates the possible applicability of this mechanism to bulk solid-state systems.
1.4.8 Limitations of dyads

One goal of RC mimics is to yield a CS state with slow and hence suppressible CR in a synthetically simple system. It appears that these two properties tend to be mutually exclusive. As ET needs to compete with other decay pathways of the initially excited state, a reasonably strong coupling is required. The factors that achieve this, e.g. a short linker, equally improve the coupling for CR. Pushing the CR further into the inverted region and hence slowing the CR rate allows lifetime extension only to a certain degree [3, 22, 31, 69, 100]. The use of spin selectivity or ion binding might provide options, but these are also limited.

So far the only feasible solution is to increase the numbers of chromophores, thereby mimicking the natural RC more closely. Stage by stage electron hopping along the redox gradient of chromophores allows for strong coupling between adjacent chromophores and hence a high rate of forward ET, but as hole and electron are spatially further separated than they would be in a dyad, the coupling for CR is weakened and thereby suppressed. Arranging chromophores in such a way obviously complicates the system, but it could be facilitated by supramolecular self-assembly [7, 110].

1.5 Experimental studies

The understanding of the processes and dynamics occurring in RC mimics and their dependence on inherent design as well as on external factors, is essential for finding the design principles of a working artificial photosynthetic system. A number of experimental techniques are therefore applied to elucidate these. Considering the coloured nature of the employed chromophores and the central mechanism of photoinduced ET, the majority of experimental measurements involve visible or near-visible light.
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1.5.1 Steady-state spectroscopy

With respect to RC mimic studies the main information derived from steady-state absorption spectra is an indication of electronic coupling between the chromophores. In the typical weak coupling limit the spectra closely resemble the sum of the spectra of isolated chromophore species. Steady-state fluorescence measurements allow one to quantify the extent of excited state quenching compared to the absence of the respective acceptor and therefore the fraction and the rate of the respective additional decay process [29, 38, 41, 65, 68, 84].

1.5.2 Time-resolved spectroscopy

As the ET events occur on very short time scales, time-resolved measurements capable of their assessment are a necessity. They allow the identification of the nature and the rates of the decay processes occurring as well as the intermediates involved. They can be broadly divided into absorption and fluorescence-based techniques and beyond this by their time resolution capability.

Time-resolved fluorescence spectroscopy

The use of time-resolved fluorescence measurements with regard to the study of RC mimics depends on how fluorescent the respective chromophores are and how well quenching can be related to the occurring processes. While they are very useful in the study of excitation EnT in e.g. light harvesting systems, the desired outcome of RC mimic excited states to decay via ET and not via luminescence imposes limitations.

The standard fluorescence-based technique for the time scales of hundreds of ps to tens of nanosecond (ns) is time-correlated single photon counting (TCSPC). It is typically carried out without wavelength resolution. The use of this technique for the study of fast ET events is limited, but it is nonetheless useful for the determi-
nation of framing parameters such as the excited state lifetimes of chromophores in isolation [22, 35, 36, 41, 55, 77].

Ultrafast fluorescence-based techniques include so-called upconversion and Kerr-gating. These allow for a time resolution down to hundreds of femtoseconds (fs) and may be wavelength-resolved. In the study of RC mimics they have found particular application in the measurement of ZnTPP $S_2$ decay and $S_1$ rise profiles [113, 120, 123, 124, 129–132].

While both TCSPC and the ultrafast fluorescence-based techniques allow for the unobstructed investigation of individual excited state decay profiles, they are obviously inapplicable to the direct detection of non-luminescent transients. The interpretation of multi-exponential decay profiles is also difficult, as the fate of the excited state cannot necessarily be resolved, especially if it is non-luminescent [49, 69, 78, 84].

**Time-resolved absorption spectroscopy**

The advantage of these techniques is that non-luminescent species can be probed [4]. A typical example of this are the usually non-luminescent radical cation and anion species of the CS state. Their spectral features are in some cases accessible by steady-state measurements of chemically oxidised or reduced chromophores or alternatively electronic structure calculations. Spectral differences also allow the distinction between different singlet and triplet excited states. The probing light’s spectral bandwidth is typically either the narrow output of a laser source or a much broader continuum.

The absorption analogue to TCSPC is ns flash photolysis. This technique has been extensively used in the study of RC mimics. As its resolution ranges from
around 10 ns up to the order of microsecond (µs) and millisecond (ms) time scales, it is mostly only applicable to systems involving very long-lived CS states and the observation of triplet states [22, 26, 30, 35, 36, 38, 41, 42, 49, 53].

The time scales accessible by ultrafast transient absorption (TA) range from a few hundred fs to a few ns. Especially in dyads with short linkers the lifetime of the CS state is too short lived (typically sub-ns) to be probed by flash photolysis [53]. As ET events typically occur at the fs to ps time scale and pump-probe type experiments using ultrafast laser pulses have evolved considerably over recent years, ultrafast TA measurements have allowed detailed studies of RC mimics, and are now the standard tool in their investigation [26, 38, 45, 51, 55, 56, 58, 65, 68, 73, 78, 85, 90, 133].

1.5.3 Auxiliary techniques

Beyond the above described spectroscopic measurements further experimental techniques have been applied to the study of the RC mimics. Their applicability depends on the system investigated.

Magnetic field effects

Applying an external magnetic field results in Zeeman splitting of a triplet state into three sub-levels. At a certain resonance field strength one of these becomes iso-energetic with an adjacent singlet state and as ET is spin selective as described above, this can affect the triplet and CS state yields in RC mimics. From the resonant field strength the magnitude of the spin-spin exchange interaction $|J|$ and hence the electronic coupling $V$ of the radical ions of the CS state can be deduced [9, 49, 73, 100].
1.5. Experimental studies

Figure 1.7: Splitting of the triplet states by an external magnetic field; adapted from [9].

**Time-resolved electron paramagnetic resonance (EPR)**

The time resolution of this technique is not as high as that of the ultrafast spectroscopic measurements, but it can give similar information on \(|J|\) and \(V\) as magnetic field effect measurements, with the additional information of the sign of \(J\), which can give information on the activation energy and hence whether CR is in the inverted region [29, 49, 53, 68, 73, 100, 104].

**Electronic structure calculations**

Computational calculations can aid RC mimic studies in several ways. As the systems typically contain a rather large number of atoms, density functional theory (DFT) is the most frequently used technique [30, 49, 63, 68, 71, 107]. The simplest use is in the visualisation of the ground state frontier orbitals of the donor and acceptor chromophores as well as the bridge and their qualitative energetic ordering [30, 51, 68].

Time-dependent DFT is used for excited state calculations [132, 134]. Similar calculations have been used for geometry optimisations in an attempt to determine the conformation of a flexible chromophore [84], although the applicability
1. Introduction

Figure 1.8: DFT calculated frontier orbital density distributions [30].

of a single gas phase optimised structure to the dynamics in solution is questionable.

Molecular dynamics simulations that include surrounding solvent molecules have been performed on a simple dyad with a long flexible linker. It was confirmed that the potential energy surface described by the dihedral angles, etc. shows few distinct minima other than the one produced by the $\pi$-$\pi$-stacking of the two chromophores. It nonetheless confirms the assumption of a distribution of conformations [71].

Recent developments in the field of applied DFT allow the calculation of driving force, reorganisation energies and electronic coupling for long range ET [68, 92, 106, 107]. This allows the study of the orientational dependence of the electronic coupling, which is experimentally hard to access in non-rigid systems.

Synchrotron measurements

The difficulty in designing large supramolecular assemblies lies in confirming that the desired structure has formed in solution or if not, what the actual structure is. Without this information further spectroscopic analysis is difficult, especially if the system shows behaviour that cannot be deduced from the individual chromophore components. Wasielewski et al. have used small- and wide-angle X-ray scattering (SAXS/WAXS) using a synchrotron source to deduce the solution struc-
tures of various π-π-stacked aggregates of covalently linked RC and LHC mimics made up of four or five chromophores (PDIs, porphyrins and phthalocyanines). In monodisperse samples the reported resolution is 2 – 3 Ångström(Å). The advantage of this technique over X-ray crystallography or theoretical gas phase calculations is that it is recorded under the same conditions (solvent, temperature) and concentrations as the typical spectroscopic experiment, thereby allowing a better correlation. It especially allows the targeting of ambiguities in orientation and distance of the chromophores [9, 80, 94, 135]. The instrumental accessibility is however a clear limitation on the more widespread use of this technique.

![Image of solution structures](image_url)

Figure 1.9: SAXS/WAXS derived solution structures (middle, right) of a π-π-stacked star-shaped pentad (left) [80].

### 1.6 Device implementation

Although the artificial photocatalytic splitting of water into oxygen and hydrogen has been achieved using a semiconductor solar cell [136], the approach of a molecular combination of light harvesting, reaction centre and redox catalytic sites to achieve the same outcome has so far not been successful. Several partial goals have however been achieved.

The combination of light harvesting chromophores relaying excitation energy to a RC mimic, in which this is converted into a CS state via ET, has been replicated
1. Introduction

frequently [1, 3, 80, 137]. The complexity of this approach ranges from a single EnT step between two chromophores preceding the first ET step, to large either π-π-stacked or dendritic arrangements of light harvesting chromophores.

Mimicking the light driven creation of a proton gradient within a bilayer as in natural photosynthesis has also been achieved and even been used to drive further chemical reactions, although the latter was performed by a natural enzyme [11, 85, 91]. The unidirectional ET of RC mimics and the ability of the orderly assembly of these on surfaces, possibly even using supramolecular rather than covalent binding between the chromophores, is currently heavily researched with regard to the implementation in various solar cell designs [23, 24, 30, 31, 59, 67]. One of the currently highest-performing dye-sensitised solar cells (12.3 % under simulated air mass 1.5 global sunlight) employs a zinc porphyrin derived RC mimic triad as the sensitising moiety bound to the TiO$_2$ substrate via a supramolecular binding motif [138].

Molecular approaches based on dye-sensitised solar cell designs aided by an external current are able to split water into O$_2$ and H$_2$ [139]. The ability to produce solar fuels in a purely molecular system akin to natural photosynthesis, rather than via the route of a semiconductor solar cell coupled to an electrolyser or an integrated variation thereof, remains elusive.

1.7 Objectives

While a considerable number of RC mimics have been investigated and many aspects of ET are well understood, there are still a number of open questions relating to both. Beyond this the challenge remains of how to apply the drawn conclusions in rational RC design and then further in successful device implementation.
1.7. Objectives

As outlined above, the influence of redox potentials and hence driving force, reorganisation energies and chromophore separation on ET are well understood. How the individual characteristics of the chromophores, e.g. their possible core-substitution, influence the ET behaviour however requires further investigation. This equally applies to the choice of binding motif, e.g. flexible or supramolecular rather than rigid and covalent, and the molecular nature of the binding moiety. Whether a less restrained and hence broader orientational distribution is conducive or detrimental to ET appears to be not conclusively addressed. While it is known that the orientation considerably affects the electronic coupling \cite{107} and restricting conformational flexibility by increasing solvent viscosity can reduce ET rates \cite{37}, current knowledge does not necessarily allow universal predictions to be made. How all these aspects affect the spin selectivity of the ET processes in a given system equally warrants further investigation.

The use of higher electronically excited states as the initial donor for ET in RC mimics has only become experimentally investigated recently. Due to the relatively small number of reported examples it is not entirely clear what the requirements are for this process to occur. Elucidating the nature of the initially formed CS state as well as the subsequent decay processes also requires further study. To answer the question whether and how this process can be utilised in a RC mimic, and thereby provide an increased redox potential within an artificial photosynthetic system or similarly within a dye-sensitised solar cell, necessitates a thorough understanding of this behaviour.

While a very large number of RC mimics have been investigated, this subsection of the vastly greater variable space was chosen mostly for reasons of synthetic feasibility. Rational design and hence synthetic pursuits require the relationship be-
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tween employed chromophores, binding motifs, binding moieties and environmental conditions, e.g. solvent and temperature, and also the observed behaviour occurring upon photoexcitation, to be fully understood and correlated.

With the increasing number of available avenues to the creation of larger and more complex chromophore assemblies by supramolecular, dendritic, polymeric and other means, understanding the behaviour of the latter systems inevitably requires understanding the properties of their smaller subunits. This obviously encompasses simple RC mimics. While the study of the latter promises progress towards the realisation of molecular artificial photosynthesis and solar fuels, it might also provide guidance in the design of related organic photovoltaic devices and the ET processes occurring within these.

The objective of the work carried out during the course of this thesis was to study a number of covalently and supramolecularly linked RC mimics to provide further insight into the factors affecting EnT and ET, with a particular emphasis on the role of porphyrin S₂ excitation. In order to resolve the processes occurring at the relevant time scales, a novel high repetition rate (RR) TA spectroscopy set-up was designed and built and the required analysis software compiled.

The contents of the subsequent chapters are as follows:

- **Experimental methods**
  The standard spectroscopic and supplementary techniques as well as the development, construction and operation of a high RR TA spectroscopy set-up and the required data analysis methods are described.

- **Untethered ZnTPP:C₆₀ complexes**
  Loosely self-assembled complexes of ZnTPP and C₆₀ are investigated with regard to processes originating from the ZnTPP S₂ state. This system is used
to exemplify the high sensitivity of the developed TA set-up.

- **A covalent ZnTPP-amino-substituted naphthalene diimide (ANDI) dyad**
  
  A ZnTPP-ANDI dyad, which is covalently linked via the latter moiety’s core-substituting amino-group, was studied in both polar and non-polar media equally with regard to the processes originating from the ZnTPP $S_2$ state.

- **Supramolecular ZnTPP:NDI complexes**
  
  Complexes of ZnTPP and NDI supramolecularly linked via N-donor moieties enabling ligand-to-metal binding were investigated with regard to the effect of the differing binding moieties on the rates of CS and CR.

- **An NDI$_2$-tin(IV) tetraphenylporphyrin (SnTPP):(OPh-BODIPY)$_2$ array**
  
  A covalent NDI$_2$-SnTPP triad axially coordinated by two phenolate-linked BODIPY chromophores was investigated with regard to the EnT and ET processes occurring upon SnTPP $S_2$-excitation.

- **Conclusion**
  
  The overall conclusions of the work carried out during the course of this project are presented and their implications on the rational design of RC mimics are discussed, especially with respect to utilising higher excited states.
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Chapter 2

Experimental methods

This section describes the experimental techniques employed during the course of this project. Particular emphasis is given to the description of the development of a previously unreported ultrafast TA set-up employing a high RR amplified laser system and a broadband probe source, and also allowing the simultaneous detection of the entire usable probe wavelength range. A hybrid approach to the global analysis of the data collected by the latter technique is also presented.

2.1 Sample preparation

The sample materials used during the course of this project were either commercially available compounds and solvents or specifically synthesised compounds. ZnTPP (Alfa Aesar) and C_{60} (Sigma-Aldrich) as well as the solvents toluene and benzonitrile (PhCN) (both Sigma-Aldrich and > 99.5 % purity) were used without further treatment. All other investigated materials were synthesised by the research group of Professor Steven J. Langford, Monash University, and were also employed as received.

Sample solutions of known concentrations were produced by weighing out typically a few hundred microgram (µg) of sample on a micro-balance (Perkin-Elmer...
2. Experimental methods

Autobalance AM-2) to a desired total and subsequent transfer to a graded volumetric flask, with solvent being added up to the exact volume. Unless otherwise stated sample solutions were made to a concentration of 100 micromolar(µM) of the principally excited species. This concentration proved both sufficient for robust experimental investigation as well as minimising sample self-aggregation in the solvents employed. All steady-state and sub-ns measurements were carried out in aerated solutions at room temperature. TCSPC measurement solutions were degassed using successive freeze-pump-thaw cycles. Sample degradation was monitored by comparing the steady-state absorption spectra before and after the experiment.

2.2 Steady-state spectroscopy

2.2.1 Absorption measurements

Steady-state absorption spectra were recorded on a spectrophotometer (Cary 50 Bio, Varian). Glass cuvettes of either 10 millimetre(mm) or 2 mm path length were used depending on sample and concentration. All absorption measurements were corrected for baseline and solvent blank. The primary purpose of steady-state absorption measurements was to confirm sample identity and integrity as well as to estimate the ground state coupling of donor-acceptor systems by comparison to the spectra of the individual chromophores.

2.2.2 Fluorescence measurements

Fluorescence spectra were recorded on a fluorimeter (Cary Eclipse, Varian) using either 10 × 10 mm or 2 × 10 mm path length glass cuvettes. In the case of the latter the excitation was directed via the short side and the emission was collected from the long side. All fluorescence measurements employed dilute solutions to allow both sufficient excitation light penetration as well as to minimise re-absorption of emitted fluorescence. Spectra were corrected for the detector wavelength response.
The purpose of these measurements was to identify and quantify quenching of excited states in the presence of further chromophore species. This was achieved by comparison with the fluorescence spectra in the absence of the latter, recorded at otherwise identical conditions.

**Weak fluorescence signals**

Samples with very low quantum yields (< 1 %) required an increase of the photomultiplier voltage from the otherwise standard 600 V to 800 V (corresponding to > 10 x sensitivity) as well as an increase in the integration time per scanned wavelength point from 0.1 s to 0.5 s to compensate for the increased noise level. Additionally a measurement of the blank solvent at the same excitation and detection settings was recorded which, combined with the sample’s absorption data, allowed for the correction of background fluorescence, Raman scatter of the excitation, as well as re-absorption. To this end the blank’s fluorescence data was scaled to account for the reduced intensity resulting from the sample absorption at the excitation wavelength, and subtracted from the sample fluorescence data. Subsequently the wavelength-dependent re-absorption was corrected, assuming an average of half the cuvette’s width as the travel of the fluorescence through the sample [1–3]. Due to the photomultiplier sensitivity a minimum difference of 5 nanometre (nm) (equal to the excitation and emission slit widths employed) had to be kept between excitation wavelength and the lowest scanned wavelength to avoid detector saturation. For samples with small Stokes shifts the acquired spectra were limited on the lower wavelength end, as excitation close to the absorption maximum was required to provide sufficient signal strength.

**2.3 Time-correlated single photon counting**

Fluorescence decays were measured using TCSPC. The excitation source employed consisted of a Ti:sapphire laser (Mira 900f, Coherent) and a cavity dumper (Pulse
2. Experimental methods

Switch, APE) pumped by a continuous wave solid state laser (Verdi V10, Coherent) producing tunable output from 700 to 900 nm with an average output power of > 10 milliwatt (mW) at 5.4 megahertz (MHz) RR. The output was passed to a second harmonic generator (Ultrafast Harmonic Generation System 5-050, Coherent) to produce > 1 mW of frequency doubled light for sample excitation. The generated fluorescence was collected at right angles and passed through a monochromator (H20, Jobin Yvon) for wavelength selection and detected by a micro-channel plate photomultiplier tube (EM100, Eldy). The electronic output of the latter was passed to constant fraction discriminator (Ortec 9307, EG&G) and collected and analysed by a photon counting card and software (T900, Edinburgh Instruments). For each experiment the instrument response function was collected separately, measuring the TCSPC signal of a scattering solution (Ludox Am-30, Sigma-Aldrich) with the monochromator set to the excitation wavelength. The data was fitted by iteratively reconvoluting the response function with a chosen decay model and minimising the \( \chi^2 \) residual error parameter using various software minimisation tools embedded in a MATLAB (Mathworks) routine written for this purpose.

2.4 Ultrafast transient absorption spectroscopy

Transient absorption (TA) spectroscopy employing a laser system capable of producing fs pulses and utilising a mechanically controlled time delay of excitation and probe pulses to achieve sub-ps (ultrafast) time resolution has found a ubiquitous application in the photochemical study of RCs and related compounds [4–26].

Both low repetition rate (RR) and high RR laser systems have been used in single- or two-colour experiments. This involves exciting with one laser source and probing with the typically narrow wavelength range of the same or a second laser source. Alternatively a spectrally selected section of a broader continuum source can be monitored as the probe. In all cases a detector without wavelength resolution is em-
ployed and the necessary noise reduction is achieved by lock-in detection [6, 27–36]. While this method can yield substantive insights and, if a second tunable laser source or several wavelength sections of a continuum source are used, can provide spectral information, it is obviously superseded by systems using a broadband probe and simultaneous wavelength resolved detection. The latter approach is now well developed using low RR systems and is a standard technique in photochemical and photobiological studies [37].

TA spectroscopy is based on measuring the difference between excited and non-excited sample absorption to retrieve the transient spectra. Therefore low RR systems greatly benefit from their high pulse energies and the resulting capability of exciting a high proportion of the sample, i.e. the creation of a sufficiently sized absorption change and hence more easily detected signal. Beyond this, the development of detectors able to record at the typical RR of 1 kilohertz (kHz) of such systems allows the separate acquisition of each probe pulse. This greatly improves sensitivity by utilising the high intensity correlation between subsequent laser pulses, and eliminates the immediate need to monitor a reference probe beam in parallel to account for fluctuations of the latter [37]. Parallel reference detection nonetheless improves the signal-to-noise ratio (S/N) further [38].

While the abundant excitation power is advantageous in these systems, it also increases the risk of unwanted processes that are sensitive to the pulse peak powers. These are typically non-linear interactions of the pump and probe pulses. They might occur within the cuvette material or the employed solvent and appear as so-called coherent artefacts (CAs) in the data at early delay times. Their minimisation is typically attempted by reduction of the pump power [37]. Typically encountered effects are two-photon absorption, stimulated Raman amplification and cross-phase modulation [6, 38–41].
2. Experimental methods

These issues are inherently minimised in high RR laser system TA set-ups due to the significantly lower pulse energies. Despite this, the amount of literature of photochemical studies describing this approach is clearly exceeded by studies employing a low RR laser system. As mentioned above, TA spectroscopy studies using a high RR system and employing a broadband probe have been described. In all cases only a small wavelength section of the probe continuum selected by a monochromator is measured at any given instant [29, 31, 35]. Spectrally as well as time-resolved data, as is routinely recorded with low RR systems, can be collected by incrementally adjusting the monochromator and repeating the measurement [29]. While this is technically feasible, the reported acquisition time per spectrum of 75 min [29] compared to a few tens of seconds in a standard multichannel broadband low RR TA set-up [37] explains the exceedingly rare use of this approach. This issue would be further exacerbated by the conflict between acquiring a sufficient number of time delay points for a kinetic analysis, typically a few hundred, and long-term sample and laser stability.

To the best of my knowledge there has been no previous description of a multichannel broadband TA set-up employing a laser system with a RR in the order of 100 kHz or more. There has been a literature reference to the use of a 40 kHz system combined with 14 detection channels, although in this case only limited experimental details are given, especially regarding the method of detection [6, 42].

During the initial stages of this project it became clear that sub-ns TA was vital for the thorough investigation of RC mimics. The intended laser source in our laboratory was a high RR system (10 − 250 kHz) and as mentioned above no description of the use of such a set-up for multichannel broadband TA spectroscopy was documented in the literature at the time. It was therefore necessary
to determine the required modifications with respect to previously described set-ups.

The following sections describe the developmental steps taken that finally resulted in a functioning TA set-up. It provides a very good S/N, minimal CAs and adaptability to solution and solid state as well as anisotropy measurements. The publications resulting from the work presented in this thesis are the first to describe the use of a high RR laser system as part of a multichannel broadband ultrafast TA spectroscopy set-up.

2.4.1 Laser system

The laser system employed for the TA experimental set-up was pumped by a solid state laser (Verdi V18, Coherent). The 18 W of 532 nm output of the latter was split to direct 6 W to a Ti:sapphire laser (Mira Seed, Coherent) and the remaining 12 W to a regenerative amplifier (RegA9050, Coherent). The seed laser output (tunable 800–830 nm, 400 mW, 76 MHz, 50 fs) was directed to an expander (EC9150, Coherent) to stretch the pulses in time to reduce their peak power before injection into the regenerative amplifier. After typically 15 roundtrips the pulses were ejected by the internal cavity dumper and the beam (> 1000 mW, 94 kHz) directed to a compressor (EC9150, Coherent) to provide pulses of < 60 fs duration on exit. Employing a 50:50 beam splitter, half of this output was directed to the probe beam generation. The other half was passed to an optical parametric amplifier (OPA) (OPA9450, Coherent), where for the purposes of this experiment only the residual second harmonic generation (SHG) frequency doubled output (400 – 415 nm, > 75 mW) was used to provide the pump beam.

During the course of this project the system described above was upgraded by insertion of a pulse shaper (MIIPS Box 640, Biophotonic Solutions) between seed laser and expander. It contains a spatial light modulator (SLM), which the
grating dispersed beam traverses twice allowing the adjustment of the spectral phase. By monitoring the SHG spectrum while iteratively optimising the internal SLM mask, the pulse shaper is able to pre-correct for pulse dispersion within the system. This allowed the compression of the final output pulses to their transform limit, specified for this system at $< 50 \text{ fs}$ and measured at ca. 46 fs.

2.4.2 Early attempts

Given that multichannel broadband detection is standard practice in current TA experimental set-ups, it was clear that this had to be the overall aim. Two-colour TA measurements, which are provenly feasible with a high RR system as described above, were therefore not attempted. The initial assumption was that the lower pulse powers and hence accordingly smaller absorption changes and signal strength could be compensated for by integrating over longer time periods and reducing noise levels by averaging.

The initial experimental layout, which is described in further detail below, utilised the residual SHG from an OPA for pump pulse provision and a sapphire-generated white light continuum (WLC) as the probe pulse source. The time delay adjustment of the pump and probe pulses relative to each other was achieved by means of a mechanical translation stage (UTS150PP with ESP300 controller, Newport). The latter varied the excitation beam’s path length between laser source and sample and thereby, due to the finite speed of light, the excitation pulse arrival times relative to those of the non-delayed probe beam pulses as well. The detector employed at this point was a standard fibre-coupled spectrometer (Maya2000 Pro, Ocean Optics), which recorded the probe beam light intensity after transmission through the concurrently excited sample.

After ensuring accurate pump and probe beam overlap within the sample and
matching probe intensity with spectrometer settings, computer controlled measurement scans were commenced. These involved collecting a previously adjusted number of spectra and recording their average, adjusting the translation stage to the next predetermined time delay and repeating this procedure until all time points were sampled. The time point vector was chosen to guarantee delay times of the probe pulses arriving both before and after the excitation pulses. This was thus a search for the so-called time zero ($\Delta t_0$), i.e. the precise time delay setting at which the pump and probe pulses arrive at the sample simultaneously. Assuming that transients are formed by the excitation, the transmitted probe light intensity should differ between before and after $\Delta t_0$ readings.

Despite extensive variation of the experimental parameters, especially the number of averaged spectra, no changes were observed. Even though increasing the latter parameter improved the S/N as expected, even at high settings the recorded intensity variation at a given time delay point was in the order of a few percent. While this was in line with the expected fluctuations of the laser source, it nonetheless meant that the sensitivity required to monitor absorption changes in the order of optical density $\times 10^{-3}$ (mOD), which is standard in current TA set-ups and necessary given the typical signal strength [6, 37], was by this method unattainable.

**Frequency noise and detection rate**

Compared to the electronic noise typically encountered in steady-state and slower time-resolved measurements, noise in the time domain has a far greater relative impact on ultrafast techniques. Minimising fluctuations arising from the laser or the sample is obviously conducive to an improved S/N. How to circumvent the residual noise once all feasible minimisation has been implemented is however rarely discussed explicitly in the ultrafast TA literature. A visit to the laboratory of Professor Eric Vauthey at the University of Geneva and further communication
2. Experimental methods

with its Scientific Collaborator Dr. Bernhard Lang, highlighted the importance of frequency noise and its relationship to the experimental detection rate.

Frequency or $1/f$ noise is frequently encountered in experimental measurements [43]. As its name implies its amplitude decreases with increasing frequency. Monitoring at a high detection rate therefore helps to avoid the low-frequency noise contributions produced by laser and sample fluctuations. In virtually all ultrafast TA measurements this is achieved by phase-sensitive detection. The signal is modulated at a high frequency typically by the insertion of a mechanical chopper into the excitation beam path. This directly provides the reference frequency for the lock-in amplifier used in non-wavelength resolving set-ups. Alternatively, this reference can be used to trigger synchronised multichannel detection. The high frequency limit to this is so-called shot-to-shot detection, i.e. the recording of a single probe pulse intensity per triggered acquisition. In this case the excitation is chopped at half the laser RR, which results in a series of acquisitions of alternatingly excited and non-excited sample measurements [6, 37, 44]. Only rarely is this explicitly termed phase-sensitive detection, though it clearly is so. While a lock-in amplifier multiplies the input signal with a sine wave at the reference frequency, shot-to-shot detection combined with modulation at half the acquisition rate is analogous to multiplication with a square wave, as the targeted signal is essentially binary and hence either on (sample excited) or off (not excited).

While for low RR set-ups the detection rate limit and hence suppression of the $1/f$ noise is dictated by the laser source, high RR set-ups are limited by the maximum acquisition rate of the detection system. Using a photodiode in combination with a lock-in amplifier and fast mechanical or acousto-optic beam modulation allows for further $1/f$ noise reduction and hence higher S/N, yet obviously lacks wavelength resolution. High-speed multichannel detection is limited by the maxi-
mum acquisition rate of the available spectrometer technology [6].

**Experimental redesign**

It became clear that a major redesign of the experimental detection system was required to achieve a sufficiently sensitive multichannel acquisition whilst using the available high RR laser source. As the spectrometer was identified as the instrumental bottleneck, the fastest commercially available detection rate system was sought. Unfortunately no system capable of directly matching even the laser system’s lowest RR setting to allow shot-to-shot detection was available. It was therefore decided to employ the fastest alternative and allow for the combined measurement of several pulses per acquisition. A fibre-coupled high-speed spectrometer (VIS-Spectrometer, Ultrafast Systems) with the required operating computer hardware acquisition card (PCI-6132, National Instruments) and triggering card (PCI-6602, National Instruments) capable of up to 9500 spectra/s was purchased for this purpose. Its implementation dictated many of the details described in the following sections and provided the strategic starting point for the experimental redesign.

**2.4.3 Experimental layout**

The optical components in both the pump and probe beam paths between laser source and sample were chosen to provide all the necessary adjustment functionality and robust day-to-day operation. At the same time they were kept at a minimum to reduce detrimental effects on pulse duration and hence time resolution due to their individual contributions to the overall group delay dispersion (GDD). For the same reason transmissive elements were kept to a minimum and various initially employed lenses replaced with focusing mirrors.

The pump and probe beam path lengths were chosen so that the \( \Delta t_0 \) position was set towards one end of the variable delay stage, thereby allowing for measurement
2. Experimental methods

of baseline data points prior to $\Delta t_0$ while still allowing for long time delays up to nearly 1 ns. The use of mostly orthogonal reflections and beam paths parallel to the grid of the optical table greatly aided robust day-to-day adjustments, as well as simplifying the beam path length measurements required as part of finding and setting the delay stage $\Delta t_0$ position.

The target acquisition rate of the spectrometer system was set at 9400 spectra/s to gain the maximum detection speed advantages while permitting a small curtailment to minimise the risk of running at the instrumental limit. The laser RR was reduced to 94 kHz to provide the triggering master signal. This value was chosen to provide an integer factor between it and the slave trigger controlled spectrometer acquisition rate. This division ratio implied that one acquisition would commence with every tenth laser pulse and that given the correct adjustment of electronic delays and spectrometer integration time, each intensity measurement would be the summed accumulation of ten probe pulses. Choosing a shorter integration time at a set acquisition rate would simply waste observable probe pulses and their potential contribution to an improved S/N. Utilising the same number of probe photons distributed over several pulses rather than one intense pulse also reduces the risk of CAs.

The desired modulation envelope for the excitation was a square wave and the probed sample should therefore be affected by either all or none of the pump pulse intensity. With the aim of sequential acquisitions coinciding with the alternating minima and maxima of this pattern a modulation frequency of half the detection rate, i.e. 4.7 kHz was required. Synchronised modulation of a 1 kHz pulse train at 0.5 kHz with a mechanical chopper is instrumentally straightforward. With the correct delay timing the passing pulses are either blocked by the centre of a blade, or pass through the centre of an opening, without risk of being clipped at an edge.
Mechanical chopping at nearly ten times this rate requires the use of a blade with a higher number of accordingly smaller fins and openings and hence reduced beam clearance. Without further modification this would have caused clipping of pulses at the beginning and end of each set of ten pump pulses and the corresponding probe pulses would have passed through an unevenly excited sample section. The excitation beam was therefore focused and re-collimated by a pair of 90° off-axis parabolic mirrors (NT47-097, Edmund Optics) and the blade of the mechanical light chopper (MC1000/MC1F60, Thorlabs) placed in the focal plane. This approach has been shown to be feasible up to modulation rates of 100 kHz [45], and combined with correct synchronisation, to prevent beam clipping. The two mirrors required careful alignment to produce a cleanly re-collimated and non-rotated outgoing beam, and led to some intensity losses as well as at least some GDD contribution compared to their absence. Despite this the alternative of using an acousto-optic modulator was deemed unnecessarily complex and without further advantage.

The pump beam polarisation was adjusted by a Berek compensator (5540, New Focus) and set to 54.7° (the magic angle) relative to that of the probe beam to remove any anisotropic distortion effects arising from molecular rotation.

Initially a 300 mm focal length lens was used to focus the pump beam towards the sample. This was replaced with a 100 mm 90° off-axis parabolic mirror to reduce the GDD from passing the pulses through glass and to provide a tighter focus. Due to the sub-unity reflectivity of the employed mirror surfaces the pump beam average power at the sample was reduced to \( \leq 20 \text{ mW} \), corresponding to an energy of approximately 200 nanojoule(nJ)/ pulse at the set RR.

Stoppered glass cuvettes (21/G/2, Starna) with a 2 mm path length were used as sample cells. A magnetic stirrer bar (MSB/6x1.5, Starna), spun within the
sample solution by an external motor mounted magnet (Magnetic Stirring System, Ultrafast Systems) and positioned as close as possible to the beam path, ensured sufficient refreshment of the probed sample volume.

The probe beam was generated by focusing the remaining fundamental 830 nm output of the laser source into a 3 mm sapphire plate (Crystalsystems) producing a broad wavelength continuum detectable by the spectrometer from approximately 430 nm to 900 nm. To ensure that this beam was fully engulfed by the pump beam within the sample its diameter had to be compressed. Initially a 200 mm focusing and 30 mm re-collimating lens pair was used, but later replaced with a gold-coated 203 mm focal length 90° off-axis parabolic mirror (50332AU, Newport) and a standard aluminium 20.3 mm focal length 90° off-axis parabolic mirror (50328AL, Newport). Due to the self-focusing occurring within the WLC generation and it being sensitive to the pulse power and spatial profile of the input beam, both parabolic mirrors were placed on translation stages to allow the adjustments required for the collimation of the output beam. The latter, 10 mm away, was directed parallel to the pump beam to ensure a minimal angle between the two after reflection off the final parabolic mirror to allow optimal overlap within the sample. After the sample position was optimised for signal strength and stability, it remained in front of the focal plane, as otherwise clearly visible fluctuations were caused within the sample solution that were detrimental to the signal stability. This non-focused overlap was equally required to ensure that the probe beam was fully engulfed by the pump beam. Beyond the sample a 100 mm lens, two mirrors and an iris were used to spatially filter the transmitted probe beam from the remaining excitation beam and direct it to a standard microscope objective-coupled 0.2 mm fibre (P200-2-UV-vis, Ocean Optics), which passed it to the spectrometer. This arrangement also greatly minimised sample fluorescence reaching the detector.
The spectrometer intensity and hence absorption change resolution increases with measured probe intensity, but is obviously limited by detector saturation. The ideal probe intensity spectrum is therefore constant over the widest possible wavelength range. The WLC had thus to be optimised and then optically filtered. To achieve the widest possible wavelength range the energy of the source fundamental beam has to be above a threshold level. A further increase raises the intensity of the WLC, but beyond a certain input energy spatial and spectral modulations of the latter occur.

While the latter did not present an immediate experimental obstacle it coincided with a decreased WLC stability and was therefore avoided. These adjustments were controlled by a neutral density filter wheel (NDFW) placed in the input beam. The second important adjustment parameter in the WLC generation was the optimisation of the input beam profile by means of an iris. The aperture diameter, the position relative to the beam path and the distance from the sapphire plate...
all affected the spectral intensities and wavelength range and required iterative adjustment together with the NDFW. While using several irises at varying positions was trialled, it was found that the most important positioning was to place the first iris at a greater distance from the WLC generation and therefore close to the laser source. This minimised the above mentioned spectral modulations, likely due to spatially filtering diffractions from the iris edges. Subsequent irises aided the optimisation, though to a lesser degree. One final iris placed after the WLC generation allowed the selection of the central continuum section of the beam profile and removal of the spectrally inhomogeneous periphery, while a NDFW allowed adjustment of the final probe intensity.

Regardless of the optimisation parameters of the WLC generation the greater part of the input beam is not converted to other wavelengths and the resulting intensity spectrum is therefore dominated by a peak at the fundamental wavelength. Reducing the intensity to avoid detector saturation would have resulted in insufficient signal over most of the wavelength range. This was addressed by using an optical shortpass filter (XIS0780, Asahi Spectra), which could be subtly angle-tuned to limit the continuum to an upper wavelength of 730–780 nm. This unfortunately not only removed the fundamental peak but also the wavelength range beyond this, and ongoing work is seeking to address this by the use of a suitable notch filter. Ideally this filtering would have occurred after the sample where the GDD caused by introducing a transmissive optical element is irrelevant for the time resolution. Increasing the probe intensity to a suitable level in the typically selected 450 – 760 nm range however implied an accordingly higher intensity at the fundamental wavelength and hence high overall probe pulse energy. This was found to cause fluctuations within the sample and therefore it required the optical filter to be positioned before the latter. A typical example of the intensity spectrum of the WLC probe beam is given in Figure 2.2.
2.4. Ultrafast transient absorption spectroscopy

The fundamental peak’s remaining shoulder was initially further reduced by placing a suitably concentrated aqueous copper sulfate solution contained in a 10 mm path length cuvette between sample and spectrometer. The subsequently introduced pulse shaper improved the conversion efficiency of the WLC generation and hence reduced the intensity discrepancy between the fundamental peak and the remaining wavelength range. This eliminated the requirement for the copper sulfate liquid filter.

2.4.4 Electronic controls

To achieve the proposed synchronised detection at one tenth and a pump beam modulation consequently at one twentieth of the RR required an electronic circuit accordingly to divide the master trigger signal provided by the laser source electronics, and provide two output signals to control the spectrometer acquisition and the mechanical chopper frequency and phase. A further requirement were individually adjustable delays of the two output signals relative to the input, to allow one to compensate for the finite time response of both the spectrometer system and the chopper driver electronics. While techniques that depend on very fast electronic triggering such as TCSPC are sensitive to the length of the cables employed due to the finite signal travel speed within the latter, the µs triggering time scales of this
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experiment were sufficiently slow to be insensitive in this respect.

After having identified the above triggering scheme, and taking into account the electronic signal requirements of the spectrometer system and the chopper driver as well as the laser source output (all in the standard transistor-transistor logic (TTL) class), the division circuit was designed with the help of Dr. Wilfred Fullagar and constructed from individual electronic hardware components. In brief, an appropriately wired binary counter chip (74HC193) is stepped up by each input trigger signal until it reaches the binary equivalent of the tenth state and produces an output signal, which resets it for the subsequent iteration via feedback through a NAND-gate (74HC00) containing circuit. This provides the raw signal for the spectrometer triggering as well as providing the input for a dual D-type flip-flop (74HC74) containing circuit, which generates one output with every second input, thereby halving the signal frequency. This represents the raw modulation trigger signal. Both raw output signals are passed through two individual 555 timer chip (NE555) containing circuits, which allow the output delay to be controlled by the use of a manually adjustable variable resistor and provide the final output signals. The overall function was confirmed by monitoring both input and output signals on an oscilloscope.

Beyond directing both output signals to their intended recipients, the modulation trigger was also passed to the spectrometer electronics. This allowed the latter to time the first detection within a series of subsequent acquisitions to coincide with the chopper blade permitting a group of ten pulses to pass. This removed the 180° phase relationship ambiguity between acquisition and modulation rate. The spectrometer integration time was set to 100 μs (ca. 9.5 × Δt_{pulse-to-pulse}) to ensure that a single detection would always be limited to ten probe pulses. By passing a small fraction of excitation scatter to the spectrometer and collecting sets of one
hundred acquisitions continuously, while monitoring the averages of all odd (pump passed by chopper) and all even (pump blocked) numbered spectra, the two time delay settings were easily corrected and set.

Figure 2.3: 94 kHz RR laser source TA triggering schematic: the laser source pulse train/ trigger signal (red) is divided by 20 and delayed to provide the light chopper input signal (dashed green) synchronising the beam modulation (green, high = beam passed/ low = beam blocked) as well as divided by 10 and delayed to provide the spectrometer trigger signal (dashed blue) initiating the acquisition (blue, high = integrated acquisition, low = read-out).

2.4.5 Acquisition algorithm

The instrumental control which coordinated user input, spectrometer acquisition, delay stage positioning as well as data processing and storage was carried out by a MATLAB operating routine created and compiled for this purpose and navigated by a graphical user interface. It comprised >2,000 lines of code and therefore in the following only parts with relevance to the experimental results are presented in a conceptual format.

Procedure 2.1 describes the collection of various constant spectral parameters required for the data processing. The measured WLC intensity fluctuation distribution was found to be asymmetrical in nature, which is likely to be the result of a combination of fluctuations within the laser source as well as passing dust
particles in the generating beam. Simply averaging a collected series of spectra would therefore be falsely biased by outliers. To eliminate these the most typical spectral result within a series, the mode spectrum, is calculated and spectra beyond a symmetrically defined range extending from the latter and quantified by the standard deviation ($\sigma$) are removed from the series. Due to the number and magnitude of outliers differing from one acquisition to another, the removal percentage varied from \textit{ca.} 0–30\% and thus substantially from the \textit{ca.} 5\% expected for a symmetric random distribution. The improvement in S/N resulting from the outlier removal was clearly noticeable yet difficult to precisely quantify, due to computational limits on the size of simultaneously acquired datasets. The procedure of outlier removal is a common tool in ultrafast TA [6, 42].

Procedure 2.2 describes the important initialisation steps taken prior to the acquisition of time-resolved data. While the constant spectral parameters acquired during procedure 2.1 were acquired at 10,000 spectra/s, scanned measurements only employed 1,000 spectra/s. Although acquiring a higher number of spectra is obviously conducive to an improved S/N, the required computational processing time increased disproportionally beyond a certain number and it was more time efficient to run multiple scans at the lower setting. Recording a higher number of separate acquisitions also proved to be a more robust tool against extreme outlier effects, as disturbances causing fluctuations beyond the time period of a single acquisition would only affect a subset. The purpose of the logarithmic spacing of the positive delay increments was to ensure a finely spaced grid at early times to capture ultrafast kinetics, while equally not over-sampling the minor changes occurring at longer delay times.

Procedure 2.3 shows the two nested loops carrying out the acquisition of the time-resolved data. The inner loop carries out the same detection and data process-
2.4. Ultrafast transient absorption spectroscopy

Procedure 2.1 Recording of background and WLC intensity before ($I_0(\lambda)$) and after ($I_{\text{nonexcited}}(\lambda)$) sample

number of spectra, $n_{\text{spectra}} \leftarrow 10,000$  \hspace{1cm} \triangleright ca. 1 s acquisition time

Ensure: all beams blocked

Spectrometer acquisition($n_{\text{spectra}}$) $\rightarrow$ collected spectra

Remove spectra $\notin \text{mode}(\text{collected spectra}) \pm 2 \times \sigma(\text{collected spectra})$

background $\leftarrow \langle \text{collected spectra} \rangle$

Ensure: probe beam unblocked, no sample inserted

Spectrometer acquisition($n_{\text{spectra}}$) $\rightarrow$ collected spectra

Remove spectra $\notin \text{mode}(\text{collected spectra}) \pm 2 \times \sigma(\text{collected spectra})$

$I_0(\lambda) \leftarrow \langle \text{collected spectra} \rangle - \text{background}$

Ensure: probe beam unblocked and sample inserted

Spectrometer acquisition($n_{\text{spectra}}$) $\rightarrow$ collected spectra

Remove spectra $\notin \text{mode}(\text{collected spectra}) \pm 2 \times \sigma(\text{collected spectra})$

$I_{\text{nonexcited}}(\lambda) \leftarrow \langle \text{collected spectra} \rangle - \text{background}$

Store( background, $I_0(\lambda)$ and $I_{\text{nonexcited}}(\lambda)$ )
Procedure 2.2 Intensity difference data $\Delta I(\lambda, \Delta t, \text{scan})$ recording - Initialisation

- number of spectra, $n_{\text{spectra}} \leftarrow 1,000$  \(\triangleright\) ca. 0.1 s acquisition time
- number of scans, $n_{\text{scans}} \leftarrow 10 \sim 20$  \(\triangleright\) depending on signal strength and stability
- maximum time delay, $\Delta t_{\text{max}} \leftarrow 20 \sim 900\text{ps}$  \(\triangleright\) depending on sample kinetics
- number of background time delays $\leftarrow 10$
- background delay times $\leftarrow -\Delta t_{\text{max}}/10 \sim -\Delta t_{\text{max}}/100$  \(\triangleright\) linearly spaced
- number of positive time delays $\leftarrow 200$
- positive delay times $\leftarrow \Delta t_0 \sim \Delta t_{\text{max}}$  \(\triangleright\) logarithmically spaced
- number of scan delay times, $n_{\text{delay times}} \leftarrow 210$
- scan delay times, $\Delta t \leftarrow \text{background delay times} + \text{positive delay times}$

Ensure: pump and probe beams overlapped at sample, modulation synchronised

Initially the outlier removal was performed separately on the excited and non-excited spectra subsets before calculating the intensity differences and the final averaging. Once the complete time range has been scanned the inner loop is completed, the translation stage is returned to the starting position, and the outer loop is moved onto the next scan upon which the inner loop commences again. After the final scan the total required acquisition is completed, and the created three-dimensional data set ($\Delta I(\lambda, \Delta t, i_{\text{scan}})$) provides the final input necessary for the generation of the target data, showing the differential absorption as a function of wavelength and time ($\Delta A(\lambda, \Delta t)$).

Initially the outlier removal was performed separately on the excited and non-excited spectra subsets before calculating the intensity differences and the final averaging. While this provided an improvement compared to no processing, at least some of the outliers in the two subsets were not in pairs of subsequent acquisitions, and therefore not taking into account the correlated nature of the noise sources. Performing the outlier removal on the intensity differences calculated from the two subsets therefore improved the S/N further by only retaining or discarding pairs of
2.4. Ultrafast transient absorption spectroscopy

**Procedure 2.3** Intensity difference data $\Delta I(\lambda, \Delta t, scan)$ recording - Scanning

For $i_{scan} \leftarrow 1, n_{scans}$ do

For $i_{delay\ time} \leftarrow 1, n_{delay\ times}$ do

Move to translation stage position $\Delta t(i_{delay\ time})$

Pause($0.1 - 3$ s) $\triangleright$ required for correct delay stage positioning

Spectrometer acquisition($n_{spectra}$) $\rightarrow$ collected spectra

nonexcited spectra, $I(\lambda)_{all\ excited} \leftarrow$ collected spectra ($1^{st}$, $3^{rd}$ ... etc.)
excited spectra, $I(\lambda)_{all\ nonexcited} \leftarrow$ collected spectra ($2^{nd}$, $4^{th}$ ... etc.)

intensity difference spectra $\Delta I(\lambda)_{all} \leftarrow I(\lambda)_{all\ excited} - I(\lambda)_{all\ nonexcited}$

Remove spectra $\notin$ mode($\Delta I(\lambda)_{all}$) $\pm 2 \times \sigma(\Delta I(\lambda)_{all})$

$\Delta I(\lambda) \leftarrow \langle \Delta I(\lambda)_{all} \rangle$

Store($\Delta I(\lambda)$) $\rightarrow \Delta I(\lambda, \Delta t(i_{delay\ time}), i_{scan})$

end scan

Move to translation stage position $\Delta t(i_{delay\ time} = 1)$

Pause(15 s) $\triangleright$ allowing delay stage resetting for next scan

end all scans
subsequently acquired excited and non-excited spectra.

The acquisition and processing time per finally recorded intensity difference spectrum was in the order of ca. 0.3 s. Given that each time delay is sampled once during every scan, the total dwell time per time delay was in the order of ca. 3–6 s. Multiplied by the number of time delays this results in ca. 20 min. Most of the experimental duration of typically 1 – 2.5 h is occupied by the time required for the precise yet slow positioning of the translation stage. The latter therefore clearly represented the instrumental bottleneck with regard to acquiring a higher number of spectra and improving S/N within a timespan limited mostly by potential sample degradation. Higher computational processing power as well as physically blocking beams during non-detection periods would allow for some if limited improvement.

While it would have been desirable to record all acquired spectra separately for a combined analysis, the computer capacities available did not allow for this. Each of the 1024 detector pixel intensities of a single spectrum is digitised to a 12 bit value, therefore resulting in a required storage of ca. 1.5 kilobyte per spectrum and hence ca. 1.5 megabyte per typical acquisition set. Given that typically up to 4,000 sets of spectra were recorded during a single experiment the resultant data volume would have been prohibitive. For this reason only the processed intensity difference spectrum calculated from one acquisition set was retained, resulting in a much more manageable data file size of ca. 20 megabyte, which included the constant spectral information as well as a record of the translation stage positioning.

2.4.6 Sample preparation

Prior to a TA measurement several aspects of the sample preparation had to be addressed. The combination of concentration and extinction coefficient had to produce an absorbance value of $> 0.3 - 1$ at the excitation wavelength in the
2.4. Ultrafast transient absorption spectroscopy

2 mm path length employed to ensure a sufficient quantity of excited species in the probed sample volume. At the same time the sample absorbance in the monitored wavelength region of the WLC of ca. 450–760 nm had to be kept below ca. 0.5 , as it would otherwise reduce the probe beam intensity reaching the detector and therefore lower the S/N at the given wavelength.

It was also found that even minimal particles of undissolved material caused strong signal fluctuations and therefore required their removal prior to measurement. All TA experiments were carried out with aerated solutions to minimise the buildup of long-lived species with lifetimes beyond the pulse separation period of ca. 10 µs.

2.4.7 Final data processing

After the data acquisition was completed, the three-dimensional \( \Delta I(\lambda, \Delta t, i_{scan}) \) data had to be converted into the desired two-dimensional \( \Delta A(\lambda, \Delta t) \) data. First the desired wavelength and time delay range had to be extracted. While the latter was usually already decided before the measurement and thus required little to no modification, the former was limited to a wavelength range with high S/N. Therefore only the intense 450 – 760 nm region of the filtered WLC was retrieved from the total 350 – 1000 nm data the spectrometer had recorded.

The next step involved visually inspecting all collected scans and discarding those with a low S/N. Causes of this were either random fluctuations that had evaded the outlier removal or occasionally sample degradation in the later scans. An optional routine developed later on in the project allowed for further outlier removal by comparing each individual datapoint with the mean value calculated from all adjacent points within the three-dimensional data set. If the discrepancy was over a certain threshold, the respective value was excluded from the final mean value calculation.
(2.1), which eliminated the data dimension described by the scan iteration.

\[ \Delta I(\lambda, \Delta t) = \langle \Delta I(\lambda, \Delta t, i_{\text{scan}}) \rangle_{i_{\text{scan}}} \] (2.1)

Equations (2.2)-(2.2b) describe how the intensity difference data acquired during the TA measurement is related to the standard format of absorption change.

\[ \Delta A(\lambda, \Delta t) = A_{\text{excited}}(\lambda, \Delta t) - A_{\text{nonexcited}}(\lambda) \] (2.2)

\[ = \log_{10} \frac{I_0(\lambda)}{I_{\text{excited}}(\lambda, \Delta t)} - \log_{10} \frac{I_0(\lambda)}{I_{\text{nonexcited}}(\lambda)} \] (2.2a)

\[ = \log_{10} \frac{I_{\text{nonexcited}}(\lambda)}{I_{\text{excited}}(\lambda, \Delta t)} \] (2.2b)

While this calculation could have been carried out at each scan point during the experiment to produce the data in its final form directly, it was decided to do this in a separate step after all acquisition had been completed. This minimised the computational processing time during the experiment and was more time efficient overall. Equation (2.4) is derived from (2.3) substituted into (2.2b) and describes the final step in the calculation of the desired \( \Delta A(\lambda, \Delta t) \) data.

\[ I_{\text{excited}}(\lambda, \Delta t) = I_{\text{nonexcited}}(\lambda) + \Delta I(\lambda, \Delta t) \] (2.3)

\[ \Delta A(\lambda, \Delta t) = \log_{10} \frac{I_{\text{nonexcited}}(\lambda)}{I_{\text{nonexcited}}(\lambda) + \Delta I(\lambda, \Delta t)} \] (2.4)

To exemplify the achievable S/N in the TA data, sample intensity and absorption difference spectra of the extensively studied ZnTPP recorded at a single time delay are given in Figure 2.4. In Figures 2.4a&b a negative intensity difference indicates an increased sample absorption resulting from the excitation. The sharp positive
signal is due to residual pump beam intensity reaching the detector, which obviously only occurs during excitation and hence results in an observed positive intensity change. The high S/N shown Figure 2.4a is a direct result of the phase-sensitive detection combined with the outlier removal and would not be possible without either. The dominant noise contribution is from the non-symmetrically distributed fluctuation of the light source rather than the detection system and hence most pronounced in the dimension of time rather than observed wavelength. Omitting the outlier removal therefore results in a fluctuation of the baseline which is severely detrimental to the S/N of the absorption changes finally calculated. In the experiment each time delay is sampled in such a manner several times during the repeated scans. This additional averaging further improves the S/N by removing long-term variations which occur on time scales longer than the 100 ms of a single acquisition of 1000 raw intensity spectra and hence evade the applied outlier removal. Figure 2.4c shows the TA change calculated from (2.4). Meaningful data can obviously only be extracted from the wavelength region in which the probe beam is sufficiently intense. The inset illustrates the level of the residual noise in this region, which is in the order of ca. 0.1 mOD. Figures 2.4d–f show the correspondingly derived kinetic profiles. The comparison of the differences between Figures 2.4a&b and those between Figures 2.4d&e clearly illustrates how averaging over several time delay scans predominantly benefits the S/N in the dimension of time rather than wavelength.

### 2.4.8 Experimental conclusion

The previous sections describe the development and operation of a multichannel broadband TA experimental set-up employing a high RR laser system. While this is not conceptually new, it is nonetheless the first demonstration of such an experimental set-up and shows that it is not limited to approaches employing low RR laser
2. Experimental methods

Figure 2.4: Example of TA difference spectra and kinetic profiles of 100 µM ZnTPP in PhCN recorded after 415 nm excitation: (a) outlier removed and averaged probe beam intensity difference between 1000 alternatingly excited and non-excited sample measurements recorded with a 10 ps time delay following excitation; (b) probe beam intensity differences averaged over 20 separate acquisitions; (c) TA spectrum calculated from (2.4); (d) kinetic profile at 580 nm of the probe beam intensity differences derived from a single time delay scan in the same manner as (a); (e) kinetic profile at 580 nm of the probe beam intensity differences derived from averaging over 20 separate time delay scans; (f) TA kinetic profile at 580 nm.

sources. Its advantages are the lower pulse energies, which minimise CAs, and its high S/N with noise levels of ca. 0.1 mOD, which compares well with the majority of studies carried out in this field. Unfortunately the set-up does not provide sufficient pump pulse energy from the tunable OPA light source to excite in the range of 500 – 700 nm, but development to this end is ongoing. Another potential disadvantage compared to low RR systems is the obviously shortened pulse separation of 10.6 µs compared to 1 ms in a 1 kHz laser source set-up, although it appears likely that sample measurements affected by this would be better addressed by ns flash
2.5. Transient absorption data analysis

In work carried out independent of this thesis, this experimental set-up was also found to be capable of investigating solid-state samples as well as providing sufficient S/N for absorption anisotropy measurements.

2.5 Transient absorption data analysis

Multichannel TA experiments produce considerable volumes of data with a typical \( \Delta A(\lambda, \Delta t) \) set containing 100,000 data points or more. This therefore requires analytical methods capable of extracting meaningful information and parameters. There are four frequently encountered contributions to the TA signal that arise from the sample excitation: ground state bleach, stimulated emission, excited state absorption and photoproduct absorption. The ground state bleach arises from the depletion caused by the excitation and results in a negative contribution taking the spectral form of the horizontally inverted steady-state absorption of the excited species. Stimulated emission originating from an excited species and induced by a probe photon increases the light intensity reaching the detector at the latter’s wavelength and therefore also results in a negative TA signal. Its spectral range and shape are similar to that of the steady-state fluorescence although also accordingly horizontally inverted. Allowed transitions to yet higher excited states give rise to excited state absorptions and produce a positive contribution. When sample excitation initiates a subsequent photochemical reaction such as photoinduced ET, the produced species might absorb in the probe wavelength range and therefore also contribute a positive signal. All these are often accompanied by CAs and inevitably some degree of noise \[6, 38, 40\].

If these contributions occur at well separated wavelengths, it is possible to assign a certain kinetic trace, which corresponds to a two-dimensional slice through the...
three-dimensional $\Delta A(\lambda, \Delta t)$ surface at a given wavelength, to an individual species. When several traces each representing a single species can be identified, they can be analysed in a combined manner allowing one to monitor and quantify the interconversion amongst them [35, 41]. This approach breaks down as soon as there is spectral overlap. In this case the analytical method needs to be capable of decomposing the individual contributions, ideally taking the entire dataset into account. Such methods are typically all termed “global analysis”, although they differ greatly in their assumptions and methodology [6, 38, 40]. Their use is widespread in TA studies of natural RCs and their synthetic mimics [4, 19, 20, 24, 26, 32, 33, 39, 42, 46–52].

This approach was found to be necessary for a substantial fraction of the TA data recorded during the course of this project. The goal was to model the data completely and thereby identify the occurring pathways as well as quantify the respective rates. The extensive spectral overlap of the ground state bleach of the various porphyrins investigated with other signal components required adaptation of existing methods. In the following a brief overview of existing methods and terminology is given, and the finally applied hybrid of global target analysis (GTA) and multivariate curve resolution by alternating least squares (MCR-ALS) presented in detail.

### 2.5.1 Method overview

Methods of globally analysing TA data can be divided into so-called soft-modelling and hard-modelling [38]. The former assumes no decay pathway model to begin with, but aims at finding the best suited description. The latter starts with several fixed models and the final selection is based on which is best suited to describe the data. Common examples of soft-modelling approaches are singular value decomposition (SVD), evolving factor analysis (EFA) and MCR-ALS. They all attempt to identify the number of components and their respective dynamic and spectroscopic characteristics, which combine to produce the overall TA data. While not
imposing a predetermined model based on *a priori* knowledge of the studied system removes bias and therefore appears desirable in principle, it equally runs the risk of producing photochemically non-feasible results. Trials of applying alternatively either SVD or the related EFA to recorded datasets of the well-characterised compound ZnTPP were both found to do this and were therefore abandoned. SVD can be used to estimate the number of components required for a successful hard-modelling approach [38, 49], but it was found that due to the ambiguity arising from the inevitable experimental noise, its results provided no advantage over the visual comparison of results from the hard-modelling approach employed later on. Whereas SVD and EFA represent rigid mathematical algorithms, MCR-ALS is an iterative routine that allows the application of constraints. The two most common are unimodality and non-negativity. Unimodality constraints apply to the component concentration profiles and only allow for one rise and subsequent decay over the entire time period. Non-negativity applies to the spectral profiles [38]. While this approach appeared promising, the negative signal contributions from the ground state bleach prominently overlapped the probed wavelength range in many of the recorded datasets, and their required inclusion in the analysis represented a severe obstacle to its application. Increasing the modelled bleach intensity at a given wavelength during the fitting had the same effect as decreasing the positive absorption contributions and therefore created an ambiguity that prevented the solvers of the fitting routine from converging on a minimum. Applying further constraints might be able to address this, but at the cost of losing the advantages of a soft-modelling approach and effectively imposing a hard model. A central aspect of the MCR-ALS method is the separation of the data into a matching number of concentration and spectral profiles and then alternatingly fixing either one or the other [38]. This concept was incorporated into the employed fitting routine described below.

Commonly employed hard model approaches are global lifetime analysis (GLA),
which is often implied by “global analysis”, and GTA, which is often abbreviated to “target analysis”. GLA involves fitting with a series of independent exponential decays. This implies the assumption of non-interacting components decaying in parallel and is therefore referred to as a parallel model. This approach has been used in the global analysis of fluorescence data, but due to TA recording absorption differences rather than absolutes, the derived spectral profiles are termed decay-associated difference spectra (DADS) rather than the otherwise employed term of decay-associated spectra [6, 40]. GLA is widely used in the study of RC mimics [4, 19, 20, 24, 37, 39, 46, 47, 50, 51]. While this approach is versatile and indeed applicable to parallel and consecutive first order reactions, the extraction of the decay pathways and their respective rate constants from the GLA of systems that do not behave in this way is difficult or at least ambiguous, especially when a high number of components is invoked [38, 52]. As the DADS usually represent a mixture of contributions, their application in the interpretation of the photochemical processes occurring in a given system is convoluted.

The model employed during GTA is a kinetic scheme and the aim is to infer concentration and spectral profiles relating to discrete photochemical species. It therefore requires solving the differential equations describing this system of pathways. The spectral profiles derived by this method are referred to as species-associated difference spectra (SADS). With the inclusion of the ground state spectrum, SADS can be converted into species-associated spectra (SAS), which are essentially the product of the wavelength-dependent extinction coefficients $\epsilon(\lambda)$ of such a species and the employed path length. Multiplied by the time-dependent concentration $c(\Delta t)$ this results in the contribution to the overall observed absorption signal. If a unidirectionally and sequentially interconverting series of concentration profiles is assumed, the analytical solution is represented by a sum of exponentials with increasing lifetimes, and the spectral profiles are referred to as evolution-
associated difference spectra (EADS). If this assumption is correct, the EADS are equivalent to the SADS. Otherwise they represent a mixture of species similar to the case of DADS. The advantage of GTA is that once the correct model is determined, it directly produces the kinetic parameters. It therefore allows for the quantitative evaluation of systems in which the decay pathways do not represent a sequential series, for example when branching into two competing decay pathways occurs [6, 38, 40]. GTA has been applied to the study of both natural and synthetic RCs and LHCs [6, 26, 32, 33, 40, 42, 48].

Despite depending on the correct choice of model, the more direct photochemical interpretation and estimation of kinetic parameters resulting from GTA appeared advantageous compared to the easier application yet harder interpretation encountered in GLA. It was therefore selected as the employed TA data analysis method. The direct application of GTA was hampered by the same issues as MCR-ALS, which were equally caused by a strong spectral overlap of the ground state bleach. The analysis method developed constituted a hybrid of these two approaches and allowed these issues to be overcome.

### 2.5.2 Data preprocessing

A prerequisite to the application of all the described methods is that the data is assumed to be bilinear, alternatively also termed “two-way” data [6, 38, 40]. In this case the three-dimensional data $\Delta A(\lambda, \Delta t)$ can be described as the product of a spectral matrix $S(\lambda, i_{\text{component}})$ and a concentration matrix $C(i_{\text{component}}, \Delta t)$, which carry a shared dimension corresponding to the total number of components $n_{\text{components}} = \sum i_{\text{component}}$ within the respective model:

$$\Delta A(\lambda, \Delta t) = S(\lambda, i_{\text{component}}) C(i_{\text{component}}, \Delta t)$$ (2.5)
This is essentially the Beer-Lambert law and here $S(\lambda, i_{component})$ can be understood as the product of a matrix made up of the extinction coefficients $\epsilon(\lambda, i_{component})$ multiplied by the scalar value of the path length $l$:

$$S(\lambda, i_{component}) = \epsilon(\lambda, i_{component})l \quad (2.6)$$

If a certain form of error, for example an independently measurable CA, is known beforehand, an additional error matrix $E(\lambda, \Delta t)$ can be introduced into (2.5) [38]:

$$\Delta A(\lambda, \Delta t) = S(\lambda, i_{component})C(i_{component}, \Delta t) + E(\lambda, \Delta t) \quad (2.7)$$

Due to the absence or minimal amplitude of CAs and a generally sufficient S/N this was not found to be necessary. The final two aspects that had to be addressed for the bilinear assumption of (2.5) to hold true were the finite time duration as well as the wavelength-dependent $\Delta t_0$ of the instrumental response function (IRF). The latter is the convolution of the pump and probe pulses and its finite width was addressed during the fitting. Due to the physical processes occurring during the WLC generation and the group delay dispersion (GDD) the probe pulses experience on their way to the sample, the temporal overlap with the pump pulses and hence $\Delta t_0$ is wavelength-dependent [37, 38, 40, 44]. This had to be corrected prior to fitting. It is possible to measure the IRF independently using a blank solvent sample or a microscope slide, although most studies assume a Gaussian shape as it simplifies the mathematical convolution during the fitting routine [32, 40]. While the same measurement can also provide the IRF’s wavelength-dependent timing, the so-called “chirp”, the precise timing depends on the penetration depth of the pump and the probe pulses into the sample, which in turn depends on the latter’s absorption profile and accordingly differs from the solvent blank. For this reason a chirp correction routine only using the raw $\Delta A(\lambda, \Delta t)$ data as an input was compiled in MATLAB. It is outlined conceptually in Procedure 2.4. A trial incorporating the chirp correction
within the iterative fitting routine was carried out, but it yielded little improvement and was therefore abandoned.

**Procedure 2.4 Chirp correction of the raw \( \Delta A(\lambda, \Delta t) \) data**

For \( \lambda_{\text{pixel}} \leftarrow \lambda_{\text{min}}, \lambda_{\text{max}} \) do

- Cross correlation( \( \Delta A(\lambda_{\text{pixel}}, \Delta t), \delta\)-function ) → cross correlation(\( \Delta t \))
- Find maximum( cross correlation(\( \Delta t \)) ) → \( \Delta t_0(\lambda_{\text{pixel}}) \)

End

Fit 3rd-order polynomial( \( \Delta t_0(\lambda_{\text{pixel}}) \) ) → chirp(\( \lambda_{\text{pixel}} \))

For \( \lambda_{\text{pixel}} \leftarrow \lambda_{\text{min}}, \lambda_{\text{max}} \) do

- Shift( \( \Delta A(\lambda_{\text{pixel}}, \Delta t - \text{chirp}(\lambda_{\text{pixel}})) \) ) → \( \Delta A(\lambda_{\text{pixel}}, \Delta t) \)

End

### 2.5.3 The kinetic model

As mentioned above the overall analysis goal was to describe the data with a photochemical model completely. While a series of sequentially occurring first-order kinetics can be analytically described by a sum of exponentials [40], the analytical solution of more complex and especially branched kinetic schemes quickly becomes lengthy. While mathematical software packages such as MATLAB are capable of calculating approximate analytical solutions, their computation and evaluation time was found to be prohibitive as regards their inclusion within the iterative fitting routine. MATLAB alternatively provides solvers that are capable of numerically integrating a system of ordinary differential equations (ODEs). These allowed the calculation of the time-dependent concentration profiles of all species contained within a certain kinetic scheme several orders of magnitude times faster than via the alternative route of first calculating the analytical solution. As both methods allow predetermining the calculated solution’s numerical accuracy, which is related to the
computational expense, they are equivalent regarding the quality of their output. For models with branching decay pathways and a higher number of components, the software derived analytical solution became unworkable and could not be used as a validation comparison. The calculated results of the standard kinetic scheme involving a reactant converting via a fast first-order decay to an intermediate, which undergoes a slow first-order decay to the final product and hence reaches finite concentration levels, were however identical to the standard analytical solution. Even the most extensive kinetic scheme employed, containing the ground state and five other components interconverting via nine first order processes, could be evaluated in ca. 0.2 s using a standard desktop machine. To ensure a negligible inaccuracy of the numerical results the calculation accuracy was set to a fractional error tolerance of $< 10^{-200}$. While this seemed excessive given the magnitude of the experimental error, it eliminated artefacts arising when the employed rate constants varied greatly in their order of magnitude, thereby causing obvious errors in the calculation. The increase in computational cost compared to a more realistic value was less than an order magnitude.

Initially this approach was only used to model the decay pathways after excitation by the pump pulse by assuming an excitation fraction $f$ and setting the starting sample portions for the initial excited state to $f$, for the ground state to $1 - f$ and zero for all others. For a complete model of the experimentally measured concentration profiles the convolution with the IRF had to be included. Convolution of the output of the ODE-solver with the typically used Gaussian approximation of the IRF [32, 40] is easily carried out in MATLAB. Carrying out three separate steps of assigning an excitation fraction and the initial conditions, solving the ODE system and convoluting with the IRF was found to be time consuming, especially during the fitting routine, which repeats these numerous times. To condense this process, Gaussian time-dependent terms describing the excitation from the ground state to
the initially excited state were included in the ODE system. This conceptually only accounts for the finite width of the pump pulse and would still require convolution with the probe pulse. Due to the convolution of two Gaussian functions resulting in a further Gaussian function with a width derived from the former two, and considering the extreme case of the convolution with a δ-function, which effectively replicates the input, the same can equally be achieved by assuming that the IRF is the result of a longer pump pulse and an infinitely narrow probe pulse. Introducing these terms into the ODE system and assigning the Gaussian width to that of the IRF rather than to that of the pump pulse, meant that the output of the ODE-solver directly represented the concentration matrix $C(i_{\text{component}}, \Delta t)$ required in the evaluation of the spectral matrix $S(\lambda, i_{\text{component}})$ as per (2.5).

2.5.4 The fitting routine

The primary goal of the fitting routine is to quantify the kinetic parameters describing the system investigated. Together with the instrumental parameters these give rise to the time-dependent concentration profiles, which multiplied by their individual spectral profiles and then combined, produce the experimentally observed $\Delta A(\lambda, \Delta t)$ data. The fitting algorithm attempts to decompose the latter by creating a model of the data from input variables, quantifying the quality of the fit to the actual data in a metric, then adjusting these variables and repeating the previous step until the optimal metric and corresponding fit is found, and the underlying spectral and kinetic parameters are determined.

Due to overlapping positive and negative spectral contributions, the wavelength-dependent signal intensity as well as the typically unknown noise variance, methods used in fluorescence decay analysis are not suited to TA data analysis [38]. As mentioned above a hybrid approach was employed. The essential component of GTA is using a system of ODEs as the description of the underlying kinetic model.
to produce the concentration matrix \( C(i_{\text{component}}, \Delta t) \), whereas using the latter to determine the spectral profiles \( S(\lambda, i_{\text{component}}) \) and iteratively alternating between the two is a central aspect of MCR-ALS. In the following the steps of initialisation, fit optimisation and final adjustments carried out within the MATLAB fitting routine are described conceptually.

After deciding on the kinetic model and its corresponding set of ODEs and including the Gaussian terms relating to excitation, the next step consisted of providing the ODE-solver with the input values of the employed rate constants and the parameters describing the Gaussian IRF. All values are constrained by selected upper and lower boundaries. Where these coincide the respective values remain fixed throughout the fitting routine, whereas all others are passed as variables to the optimisation algorithm. The latter employed two differing iterative minimisation methods. A standard genetic algorithm, which is not gradient-following, samples the available multidimensional variable space to coarsely locate the global minimum, upon which a trust-region-reflective algorithm follows the local gradient to determine its precise position, and therefore provide the variable combination producing the best fit to the data. Both methods are individually available as standard subroutines in MATLAB. Given a sufficiently large sample population of variable combinations a genetic algorithm resists convergence on a local rather than the global minimum, but due to its random nature the precise localisation requires many iterations. The trust-region-reflective gradient algorithm converges much more rapidly, but is therefore prone to convergence on local minima. Using both methods in sequence combined their advantages and optimised the overall time efficiency.

The fitting algorithms are passed a non-analytical function which converts the fixed and variable input values into a single output metric relating to the quality of the fit. As described above the first step is the calculation of \( C(i_{\text{component}}, \Delta t) \).
Due to the total of all component fractions within the kinetic model being conserved at all times the latter is a rank-deficient matrix, i.e. any fraction can be deduced by deducting all others from the total. The result of this is that there is an infinite yet related number of spectral profile matrices $S(\lambda, i_{\text{component}})$ that multiplied by $C(i_{\text{component}}, \Delta t)$ as per (2.5) reproduce the identical fit surface resembling $\Delta A(\lambda, \Delta t)$. The photochemically correct set of SAS can be found by setting the spectral profile of the ground state bleach to the negatively inverted equivalent of the steady-state sample absorption spectrum of the excited moiety [40]. Due to $C(i_{\text{component}}, \Delta t)$ being a non-square matrix ($n_{\text{components}} \neq \sum i_{\text{delay time}}$) its Moore-Penrose pseudoinverse $C^+(\Delta t, i_{\text{component}})$ is used to determine $S_{\text{initial}}(\lambda, i_{\text{component}})$:

$$S_{\text{initial}}(\lambda, i_{\text{component}}) = \Delta A(\lambda, \Delta t) C^+(\Delta t, i_{\text{component}})$$  \hspace{1cm} (2.8)

$S_{\text{initial}}(\lambda, i_{\text{component}})$ is then converted to the final $S(\lambda, i_{\text{component}})$ by subtracting the difference between the initially calculated spectral profile of the component corresponding to the ground state bleach $S_{\text{initial}}(\lambda, i_{\text{ground state bleach}})$ and the negatively inverted and appropriately scaled ground state absorption spectrum $A_0(\lambda)$ individually from all components within $S_{\text{initial}}(\lambda, i_{\text{component}})$:

$$\Delta_{\text{correction}} = S_{\text{initial}}(\lambda, i_{\text{ground state bleach}}) - A_0(\lambda)$$  \hspace{1cm} (2.9)

$$S(\lambda, i_{\text{component}}) = S_{\text{initial}}(\lambda, i_{\text{component}}) - \vec{n}_{\text{components}} \Delta_{\text{correction}}$$  \hspace{1cm} (2.10)

The correct scaling of $A_0(\lambda)$ can be derived from the ground state bleach intensity at early times and can be used to estimate the extinction coefficients of the other SAS.

Once $S_{\text{initial}}(\lambda, i_{\text{component}})$ has been evaluated, it is multiplied by $C(i_{\text{component}}, \Delta t)$
to produce the fitting surface $F(\lambda, \Delta t)$:

$$F(\lambda, \Delta t) = S(\lambda, i_{\text{component}}) C(i_{\text{component}}, \Delta t)$$  \hspace{1cm} (2.11)

The next step involves calculating an appropriate residuals matrix $R(\lambda, \Delta t)$ that can be subsequently summarised over both dimensions to provide the overall lack-of-fit (LOF) metric. Due to the overlapping positive and negative signal contributions, unlike the $\chi^2$ statistics used in the analysis of TCSPC data, the signal intensity at a given datapoint within $A(\lambda, \Delta t)$ cannot be employed [40]. Visual inspections of $A(\lambda, \Delta t)$ clearly show that the dominant noise variance arises from fluctuations in time rather than wavelength, indicating that the spectrometer noise is significantly lower than variations related to the laser intensity. The wavelength-dependent variance $V(\lambda)$ is therefore calculated at each $\lambda_{\text{pixel}}$ value of $A(\lambda, \Delta t)$ to appropriately scale the squared difference between the latter and $F(\lambda, \Delta t)$ [38]:

$$R(\lambda, \Delta t) = \left( \frac{A(\lambda, \Delta t) - F(\lambda, \Delta t)}{V(\lambda)} \right)^2$$  \hspace{1cm} (2.12)

$$\text{LOF} = \sum_{\lambda} \sum_{\Delta t} R(\lambda, \Delta t)$$  \hspace{1cm} (2.13)

Once the LOF has been evaluated, the respective optimisation algorithm attempts to minimise this value by iteratively varying the input variables, until a convergence criterion is met and the best fit to $A(\lambda, \Delta t)$ has been found. The input variable values of the final iteration represent the sought after kinetic parameters. To maximise the time efficiency the fitting routine was designed to allow for parallel computing when using a multi-core machine. Due to the dataset-dependent magnitude of the LOF, the fit quality is best assessed by visual inspection of $R(\lambda, \Delta t)$ to ensure a random non-systematic distribution of the residuals [38]. The outline of the the non-analytical function calculating the LOF is given in procedure 2.5 and an overall schematic overview of the fitting routine is shown in procedure 2.6.
2.5. Transient absorption data analysis

Procedure 2.5 Evaluating the LOF to $\Delta A(\lambda, \Delta t)$ of a fit surface $\Delta F(\lambda, \Delta t)$ derived from input values passed to a kinetic model described by $n_{\text{components}}$ ODEs containing $n_{\text{rates}}$ first-order rate constants and three IRF parameters (amplitude, timing and width of Gaussian)

- kinetic model $\leftarrow n_{\text{components}}$ ODEs
- rate constants $\leftarrow n_{\text{rates}}$ input values
- IRF parameters $\leftarrow$ 3 input values

$\text{ODE-solver}(\text{kinetic model, rate constants, IRF parameters, } \Delta t)$ $\rightarrow$ $C(i_{\text{component}}, \Delta t)$

$\text{Moore-Penrose pseudoinverse}(C(i_{\text{component}}, \Delta t)) \rightarrow C^+ (\Delta t, i_{\text{component}})$ ▷ (2.8)

$S_{\text{initial}}(\lambda, i_{\text{component}}) \leftarrow \Delta A(\lambda, \Delta t) C^+ (\Delta t, i_{\text{component}})$ ▷ (2.8)

$SAS(S_{\text{initial}}(\lambda, i_{\text{component}}), A_0) \rightarrow S(\lambda, i_{\text{component}})$ ▷ (2.9) & (2.10)

$\text{Fit surface}(S(\lambda, i_{\text{component}}), C(i_{\text{component}}, \Delta t)) \rightarrow F(\lambda, i_{\text{component}})$ ▷ (2.11)

$\text{Data wavelength variance}(A(\lambda, i_{\text{component}})) \rightarrow V(\lambda)$ ▷ (2.12)

$\text{Residuals}(A(\lambda, i_{\text{component}}), F(\lambda, i_{\text{component}}), V(\lambda)) \rightarrow R(\lambda, i_{\text{component}})$ ▷ (2.12)

$\text{Output}(R(\lambda, i_{\text{component}})) \rightarrow \text{LOF}$ ▷ (2.13)
2. Experimental methods

Procedure 2.6 Fitting routine overview

**Setting boundaries** (rate constants, IRF parameters) → fixed inputs & variable inputs

For $n_{\text{iterations}}$ do

Genetic algorithm ($A(\lambda, i_{\text{component}})$, fixed inputs, variable inputs) → varied inputs

▷ typically $n_{\text{iterations}} = 20$

End

variable inputs ← varied inputs

While $\text{LOF}_{i+1} < \text{LOF}_i$ do

Gradient algorithm ($A(\lambda, i_{\text{component}})$, fixed inputs, variable inputs) → varied inputs

▷ typically $n_{\text{iterations}} \geq 100$

End

fit values ← varied inputs

Output (fit values, $F_{\text{opt}}(\lambda, i_{\text{component}})$, $R_{\text{opt}}(\lambda, i_{\text{component}})$, $\text{LOF}$)

Output ($C_{\text{opt}}(i_{\text{component}}, \Delta t)$, $S_{\text{opt}}(\lambda, i_{\text{component}})$)
2.5.5 Parallel analysis of multiple datasets

The above described fitting routine was extended to allow for the combined analysis of several $A(\lambda, i_{\text{component}})$ datasets. The idea was to aid the spectral decomposition by applying the constraint that the spectral features of certain components are shared between datasets, although their concentration profiles might differ. This concept is referred to as a second-order global analysis and makes use of the bilinear assumption described in (2.5) [38].

For datasets where spectrally shared components could be guaranteed, for example when the same sample was recorded over two differing time ranges, the routine functioned as expected. For most of the RC mimic systems investigated during the course of this project, it however appeared that the spectral profiles of the non-ground state components varied significantly in comparison to those of the isolated chromophores. While this was unsurprising, given the desired property of a strong excited state coupling between the donor and acceptor moieties to facilitate ET, it indicated that this method was limited to dataset combinations of minimally differing samples.

2.5.6 Concluding remarks

All of the above described TA data analysis method constitutes the final product of several previous iterations. Although solely carried out in a MATLAB code environment, it allowed for facile modification of the kinetic model and input value boundaries as well as the desired graphical output. The typically most time consuming part of the data analysis was the determination of the most appropriate kinetic model, whereas the fitting routine typically converged within $< 10$ min. While both GTA and MCR-ALS have been abundantly applied, the hybrid detailed here has to the best of my knowledge not been described elsewhere. Its advantages lie in the application to $A(\lambda, i_{\text{component}})$ datasets with extensive overlap of positive and nega-
tive signal contributions, as well as the straightforward photochemical significance of the derived kinetic parameters. The integration of data acquisition as well as analysis within a single fully user-defined software framework greatly benefited its optimisation as well as future versatility.

2.6 Electronic structure calculations

DFT calculations of isolated chromophores were carried out as a supplementary tool to allow the visualisation and approximate energetic quantification of their highest occupied molecular orbital (HOMO) and lowest unoccupied molecular orbital (LUMO) frontier orbitals. They were all performed using commercially available software (Gaussian03 Revision B.04, Gaussian Inc.) installed on a standard desktop machine using the standard B3LYP/6-31G(dp) level of theory.
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2. References


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Chapter 3

Untethered $\text{ZnTPP:C}_60$ complexes

The work presented in this chapter was part of a collaboration with the research group of Professor Ronald Steer, University of Saskatchewan, Canada, and resulted in a joint publication titled “Photophysics of untethered ZnTPP-fullerene complexes in solution” [1]. The goal of this project was to discern the decay processes of ZnTPP excited into its $S_2$ state while non-covalently linked to $C_{60}$ in solution. While it has been shown that in this system on longer time scales ET can occur between the ZnTPP and $C_{60}$ triplet states [2], the processes occurring on the ultrafast time scale had previously not been investigated. Our interest lies in utilising non-coherent photon upconversion via triplet-triplet annihilation to yield $S_2$ as the final product and donor for subsequent ET, with the goal of improving the overall efficiency of organic photovoltaic devices. This investigation coincided with the completion of the TA set-up and is therefore used here to exemplify the experimental system’s sensitivity and minimal CA contribution. The TA data analysis method described in 2.5 is demonstrated on $S_2$-excited ZnTPP in toluene and PhCN, which represents the comparison data for investigations described in this as well as subsequent chapters. The non-polar toluene and polar PhCN were chosen as the employed solvents due to the solubility of ZnTPP and their respective polarities.
3. Untethered ZnTPP:C₆₀ complexes

3.1 ZnTPP

3.1.1 TA spectra in toluene

Figures 3.1 and 3.2 show the processed TA datasets of 100 µM ZnTPP in toluene excited at 415 nm recorded up to 900 ps and 16 ps after ∆t₀. The TA spectra are the product of several positive and negative signal contributions. The dominant features are the S₁ state absorption, which is most pronounced in the 450 – 600 nm region and gradually decays with a 1.9 ns lifetime, and the overlapping ground state bleach, which produces a strong negative signal at 550 nm and a smaller minimum at 590 nm. Stimulated emission from S₁ contributes to the latter as well as producing a further minimum at 650 nm. A growing contribution with a maximum intensity at 480 nm is due to the absorption of the T₁ state formed by ISC from S₁ and hence its rise mirrors the latter’s decay. Even though the delay stage range did not allow the quantification of the T₁ lifetime in the investigated sample, the flat baseline prior to ∆t₀ clearly shows that it was sufficiently quenched by the aerated solution conditions to decay fully within the pulse separation period (ca. 10 µs, cf. 2.4). A very short-lived component with a lifetime of ca. 1.4 ps most clearly discernible at 650 nm and more clearly resolved in Figure 3.2 is due to the S₂ state absorption [3, 4]. Its decay via near quantitative IC to S₁ can be observed by the latter’s matching rise at 575 nm.

The residual noise level in these datasets is in the order of ca. 0.1 mOD and more significant in the dimension of time rather than wavelength, due to the detector noise contribution being small compared to that caused by the laser source fluctuations. This observation holds true for all TA datasets presented in this and following chapters. The low noise levels compare well with the data recorded with typically 1 kHz RR laser source set-ups presented in the current literature, especially given the single-channel detection without the use of a parallel reference channel.
Notable is also the absence of any discernible CAs at times close to $\Delta t_0$. The early rise and decay dynamics of the sample compound can therefore be observed without any obscuring contributions. While this was initially attributed solely to the low pulse powers employed, subsequent measurements showed that a low sample absorption at the excitation wavelength could lead to a short CA contribution with a small and relatively even magnitude across all probed wavelengths. Compensating by increasing sample concentration was limited by the detrimental decrease in transmitted probe beam intensity, which consequently reduced the S/N, as well as by potential sample aggregation. A high absorption at the excitation wavelength obviously implied a shortened penetration depth of the pump beam and therefore required careful adjustment of the probe beam to ensure full overlap. Altering the excitation wavelength was limited by the feasible wavelength tuning range of the employed laser source.

Figure 3.1: TA spectra of 100 µM ZnTPP in toluene recorded up to 900 ps after 415 nm excitation.
Application of the developed hybrid global target analysis method

The decay processes of Soret band ($S_2$) excited ZnTPP in solution are well established [4, 5]. To exemplify the hybrid GTA as the employed data analysis method, the decay scheme shown in Figure 3.3a is applied to the data shown in Figure 3.1. The results shown in the remainder of Figure 3.3 are the optimal fit concentration and spectral profile matrices, which provide the kinetic parameters and the decomposed spectral profiles. Even though the effect of the radiative decay rates on the overall fit is small compared to those of the non-radiative pathways, their inclusion demonstrates the application of the developed analysis method to branched decay schemes.

3.1.2 TA spectra in PhCN

Figures 3.4 and 3.5 show the processed TA datasets of 100 µM ZnTPP in PhCN excited at 415 nm recorded up to 900 ps and 16 ps after $\Delta t_0$. The spectra are similar to those recorded in toluene. The main difference is a ca. 10 nm red-shift of the features associated with $S_2$, $S_1$ and the ground state bleach, as well as an increase of the $S_1$ absorption between 500 and 650 nm. As a result the absorptions
3.1. ZnTPP

Figure 3.3: Hybrid GTA applied to the TA data of 100 µM ZnTPP in toluene excited at 415 nm displayed in Figure 3.1: (a) ZnTPP kinetic decay scheme used in hybrid GTA; (b) absorption spectrum of ZnTPP in toluene; (c) fitted concentration profiles contained in $C(i_{\text{component}}, \Delta t)$: $S_2$ in blue, $S_1$ in green, $T_1$ in black and $S_0$ in grey; (d) component SAS contained in $S(\lambda, i_{\text{component}})$: $S_2$ in blue, $S_1$ in green, $T_1$ in black and $S_0$ in grey (cf. (2.5.4)); (e) - (h) matrices resulting from multiplying the concentration profiles with their respective spectral profiles, which combined reproduce the experimentally observed TA data.
of the decay of $S_1$ and the rise of $T_1$ in the 450 – 500 nm region are more clearly discernible.

Figure 3.4: TA spectra of 100 µM ZnTPP in PhCN recorded up to 900 ps after 415 nm excitation.

Figure 3.5: TA spectra of 100 µM ZnTPP in PhCN recorded up to 16 ps after 415 nm excitation.
3.1. ZnTPP

(a) Absorption spectrum in PhCN
(Q-band region shown ×10 in green)

(b) $C(i_{\text{component}}, \Delta t)$

(c) $S(\lambda, i_{\text{component}})$

(d) $S_2$ matrix

(e) $S_1$ matrix

(f) $T_1$ matrix

(g) $S_0$ bleach matrix

Figure 3.6: Hybrid GTA applied to the TA data of 100 µM ZnTPP in PhCN excited at 415 nm displayed in Figure 3.4: (a) absorption spectrum of ZnTPP in PhCN; (b) fitted concentration profiles contained in $C(i_{\text{component}}, \Delta t)$: $S_2$ in blue, $S_1$ in green, $T_1$ in black and $S_0$ in grey; (c) component SAS contained in $S(\lambda, i_{\text{component}})$: $S_2$ in blue, $S_1$ in green, $T_1$ in black and $S_0$ in grey (cf. (2.5.4)); (d) - (g) matrices resulting from multiplying the concentration profiles with their respective spectral profiles, which combined reproduce the experimentally observed TA data.
3. Untethered ZnTPP:\textsubscript{C\textsubscript{60}} complexes

3.2 Investigation of untethered complexes

3.2.1 Collaborator work

While the TA measurements were carried out in our laboratories, all steady-state and time-resolved fluorescence experiments were performed by our collaborator mentioned above. Steady-state absorption spectra of mixtures of the two compounds showed no substantial difference in peak wavelength values or molar absorptivity compared to the sum of the spectra collected independently. This implied that the wavelength-dependent extinction coefficients of complexed and uncomplexed ZnTPP are very similar and selective excitation is not possible. Steady-state fluorescence experiments showed that both the ZnTPP \textsubscript{S\textsubscript{1}} and the \textsubscript{S\textsubscript{2}} emissions were quenched by addition of \textsubscript{C\textsubscript{60}}. The extent of quenching as quantified from Stern-Volmer plots (that can be identified with the binding constant) was significantly higher for \textsubscript{S\textsubscript{2}} (ca. 3.2 \times 10^{3} \text{ molar(M)}^{-1}) compared to \textsubscript{S\textsubscript{1}} (ca. 0.5 \times 10^{3} \text{ M}^{-1}) despite the vastly shorter lifetime \cite{1}. This indicated that the \textsubscript{S\textsubscript{2}} quenching process has to occur at a very rapid rate $\gg 10^{12} \text{ s}^{-1}$ to compete with the IC to \textsubscript{S\textsubscript{1}}. Beyond this, further comparison of \textsubscript{S\textsubscript{1}} emission intensities after either \textsubscript{S\textsubscript{2}} or \textsubscript{S\textsubscript{1}} excitation indicated that this process does not reform \textsubscript{S\textsubscript{1}} quantitatively.

Time-resolved fluorescence measurements of the \textsubscript{S\textsubscript{2}} decay and \textsubscript{S\textsubscript{1}} rise via the upconversion method on the ps time-scale and of the \textsubscript{S\textsubscript{1}} decay via TCSPC on the ns time-scale on the compound mixtures only provided lifetimes equivalent to those recorded of isolated and uncomplexed ZnTPP. This suggested that the observed fluorescence from the compound mixtures originates solely from the uncomplexed species, while the quenching of both the \textsubscript{S\textsubscript{1}} and \textsubscript{S\textsubscript{2}} states within the complexes occurs both rapidly compared to their respective lifetimes and also yields non-emissive products.
It has been shown previously that given suitable electronic states in a nearby acceptor both EnT [6] and ET [3, 4, 7, 8] can occur from the ZnTPP $S_2$ state. The goal of the TA measurements carried out in our laboratories was to determine which of these two processes was responsible for the observed quenching by identifying the product species. ET from $S_2$ would form the ZnTPP$^{\bullet+}$ radical cation and the $C_{60}^{\bullet-}$ radical anion, both of which are spectrally well-known [2, 9]. Unfortunately the developed TA set-up did not allow for detection in the near-infrared required for the observation of $C_{60}^{\bullet-}$ and the focus shifted onto investigating the presence of the ZnTPP$^{\bullet+}$ radical cation.

3.2.2 Sample preparation

To ensure identical concentrations in both their individual samples as well as in the mixture, stock solutions of 200 $\mu$M ZnTPP and 2 millimolar (mM) $C_{60}$ in toluene were combined with either equal parts of neat solvent or alternatively each other to yield accordingly halved concentrations. Hence within the mixture in toluene the ratio of ZnTPP to $C_{60}$ was 1:10. While this ratio still leaves a considerable fraction of uncomplexed ZnTPP, significantly higher concentrations of $C_{60}$ are severely limited by solubility. In PhCN the same procedure was used equally to yield 100 $\mu$M concentrations of ZnTPP, while the even lower solubility limited the final $C_{60}$ concentrations to 0.2 mM and thus an even lesser 1:2 excess within the mixture.

3.2.3 TA measurements

Due to the limited solubility of $C_{60}$ in both toluene and PhCN as well as its very moderate binding to ZnTPP within the complex, it was inevitable that TA measurements of the mixture would observe a combination of both complexed and uncomplexed species. While the supramolecular assembly without a tethering unit allows for a range of intermolecular distances within the complexes, the instantaneous excitation and the rapid quenching rate prevent any significant dynamic
motion occurring during the investigated time-span. It therefore simplifies the analysis by excluding the complication of having to account for the effect of an intermolecular distance distribution as discussed by Mataga et al. [3].

The approach taken in the subsequent measurements was to record the mixture and then subtract the excitation wavelength absorption-corrected datasets of the isolated species with the goal of identifying significant deviations caused by the addition of C\textsubscript{60} in the produced difference spectra. The employed excitation wavelength remained 415 nm throughout. To ensure identical experimental conditions, the sets of measurements providing the input for the calculation of the respective difference spectra were recorded consecutively without any parameter adjustment.

\textbf{C\textsubscript{60} and ZnTPP:C\textsubscript{60} mixture in toluene}

The transient spectra of C\textsubscript{60} in toluene in Figure 3.7a show a long-lived, broad absorption with a small maximum at 530 nm clearly assignable to its S\textsubscript{1} state. The transient spectra of the ZnTPP:C\textsubscript{60} mixture in toluene presented in Figure 3.7b are very similar to those of ZnTPP without C\textsubscript{60} present (Figure 3.2). However, the band at the blue end of the detection range is significantly reduced while the amplitude in the region above 500 nm and especially above 550 nm is markedly increased. To further quantify this observation, the relative excitation wavelength absorbance (A\textsubscript{ex})-corrected transient spectra of the individual species were subtracted from the spectra of the mixture:

$$\Delta = \text{ZnTPP : C}\textsubscript{60} - \text{ZnTPP} \cdot \frac{A_{ex}(\text{ZnTPP})}{A_{ex}(\text{ZnTPP : C}\textsubscript{60})} - \text{C}\textsubscript{60} \cdot \frac{A_{ex}(\text{C}\textsubscript{60})}{A_{ex}(\text{ZnTPP : C}\textsubscript{60})}$$ (3.1)

It should be noted that due to absorbances of the mixture equating to the sum of those of the two components (cf. 3.2.1), this calculation would result in no differences if there were no interaction between them. The difference spectra (\(\Delta\)) resulting from the measurements in toluene are presented in Figure 3.7c. Because the absorbance of
the mixture at the excitation wavelength is dominated by the ZnTPP Soret band (ca. 90 %) and the transient absorption of C<sub>60</sub> excited at this wavelength is considerably smaller than that of ZnTPP, they are dominated by differences due to the latter. There is a reduction of amplitude below 490 nm and two relatively long-lived bands centred at 510 and 560 nm are clearly discernible. Scans over a longer time delay range (up to 900 ps) show barely any decay in these bands, indicating a lifetime of \(\gg 1\) ns. Further, an extremely short-lived (< 1 ps) component centred at 650 nm can be observed. The kinetic trace at this wavelength shown in Figure 3.7d shows the rapid decay of this component to the level of the overlapping much longer-lived band extending from 560 nm to beyond the upper probe wavelength range limit. Exact quantification of the rate of this decay is limited by the finite width of the IRF, but it is clearly considerably faster than the ca. 1.4 ps rate of decay of the \(S_2\) state of ZnTPP itself. Its rise is indistinguishable from the IRF and the rate must therefore be in the order of ca. \(10^{13}\) s\(^{-1}\), which places it in the diffusion-limited barrierless region for ET [10]. It is therefore consistent with the rate requirements of the quenching process derived from the steady-state ZnTPP \(S_2\) fluorescence quenching experiments performed by our collaborator.

**C<sub>60</sub> and ZnTPP:C<sub>60</sub> mixture in PhCN**

The transient spectra of C<sub>60</sub> in PhCN in Figure 3.9a are yet again similar to those recorded in toluene, showing a broad, featureless and long-lived absorption with a minor maximum around 530 nm. The sub-ps component with a maximum absorption around 560 nm has a kinetic profile very similar to that reported of C<sub>60</sub> embedded in argon matrices and excited as well as probed at 384 nm [11]. The authors of this investigation partially attribute it to be a CA and suggest the possibility that it might be observing a fast intramolecular relaxation from a highly excited singlet state manifold to the molecule’s \(S_3\) state. In a later investigation by the same authors studying a very similar system using neon instead of argon
3. Untethered ZnTPP:C\textsubscript{60} complexes

Figure 3.7: (a) TA spectra of 1 mM C\textsubscript{60} in toluene recorded up to 16 ps after 415 nm excitation; (b) TA spectra of 100 µM ZnTPP plus 1 mM C\textsubscript{60} in toluene recorded up to 16 ps after 415 nm excitation; (c) absorbance adjusted difference spectra resulting from combining the data from Figure 3.2 as well as (a) and (b) according to (3.1); (d) kinetic profile of (c) at 650 nm.
matrices with a slightly increased excitation and probe wavelength of 402 nm, a similar kinetic profile is once again reported, although its fast component is completely dismissed as a CA [12]. Another group reported the onset of C\textsubscript{60} aggregate formation in PhCN at concentrations below those employed in the measurements presented here, and the observation of a fast relaxation process (< 2 ps) via TA measurements attributed to intermolecular ET, although no further details are provided [13]. Despite the abundant use of C\textsubscript{60} as a molecular building block in numerous photophysical studies, there appears to have been no further investigations in the past decade into the clarification of this fast decay process.

![Kinetic profiles of TA spectra](image)

Figure 3.8: Kinetic profiles of TA spectra of (a) 1 mM C\textsubscript{60} in toluene and (b) 0.2 mM C\textsubscript{60} in PhCN both after 415 nm excitation.

Due to the low absorbance (< 0.1) resulting from the low extinction coefficient of the sample at the excitation wavelength, the contribution of a CA to the fast component observed here cannot be fully excluded. The CA signal measured in the blank solvent under the same conditions was however considerably lower in amplitude and relatively constant across the entire probe wavelength range. The
intensity and the spectral profile therefore suggest that the sub-ps signal arises at least to some extent from C$_{60}$. Beyond this, the kinetic profiles shown in Figure 3.8b across all wavelengths show no discernible relative changes beyond 10 ps, but there is a distinct decay in the region below 575 nm and a matching rise in the region above during the first few ps. The kinetic profiles of the transient spectra of C$_{60}$ in toluene shown in Figure 3.8a display more subtle changes over this time period that are, interestingly, inverted compared to those observed in PhCN, i.e. a rise below and a decay above 575 nm. The clarification of the decay processes of photoexcited C$_{60}$ in both PhCN and toluene warrants further investigation, but was beyond the scope of the work presented here. A preliminary analysis would however suggest that the dynamics observed here during the first few ps arise from possibly multiple C$_{60}$ relaxation processes. The absence of this observation within the transient spectra recorded in toluene, where no aggregation of C$_{60}$ is expected at the employed concentrations, hints at intermolecular interactions as previously alluded to [13].

As with the measurements in toluene, the transient spectra of the ZnTPP:C$_{60}$ mixture in PhCN shown in Figure 3.9b mostly resemble those of ZnTPP. However, the absorbance corrected subtracted spectra once again derived via (3.1) and shown in Figure 3.9c clearly show the key differences. There is evidence of long-lived species not decaying within the excitation pulse separation period of the experiment (ca. 10 µs), despite measuring in aerated solution. The spectral features recorded prior to $\Delta t_0$ match those recorded at any point beyond in all but total amplitude, indicating that the prominent bands at 530, 580 and 625 nm are due to an extremely long-lived species. On the time scale of this measurement they remain essentially constant. Much less obvious than in the toluene mixture measurement, but nonetheless discernible, remains an again very short-lived component spectrally ranging from 600 to 680 nm. The kinetic trace at 660 nm presented in Figure 3.9d
3.2. Investigation of untethered complexes

(a) $C_{60}$

(b) ZnTPP + $C_{60}$

(c) Absorbance adjusted difference spectra

(d) Kinetic trace at 660 nm

Figure 3.9: (a) TA spectra of 0.2 mM $C_{60}$ in PhCN recorded up to 16 ps after 415 nm excitation; (b) TA spectra of 100 µM ZnTPP plus 0.2 mM $C_{60}$ in PhCN recorded up to 16 ps after 415 nm excitation; (c) absorbance adjusted difference spectra resulting from combining the data from Figure 3.5 as well as (a) and (b) according to (3.1); (d) kinetic profile of (c) at 660 nm.
shows its rapid decay overlapping with the longer-lived components. Although the exact quantification of both its rise and decay was again limited by the IRF, a qualitative comparison with the related trace recorded in toluene shown in Figure 3.7d suggests a slower decay rate, while the rate of the rise can again only be estimated to be close to diffusion-limited.

3.2.4 Interpretation

Collaborator work

Taking the excited state energies, spectral overlaps and redox parameters of this system into account, both EnT and ET are conceivable upon ZnTPP $S_2$ excitation. As the EnT mechanism, Förster-type can be excluded due to small spectral overlap and low oscillator strength of the relevant $C_{60}$ transitions, leaving Dexter-type as the alternative. While no $C_{60}$ emission was observed in steady-state measurements, the small complexed fraction and small quantum yield did not allow for a definitive conclusion. The interpretation of the quenching and time-resolved fluorescence measurements indicated a static quenching upon both $S_1$ and $S_2$ excitation, with rates rapid compared to the uncomplexed ZnTPP lifetimes. For quenching from $S_2$ this hence implied a rate of $\gg 10^{12}$ s$^{-1}$. Consideration of the ZnTPP $S_1$ and $S_2$ molecular orbital properties, as well as the $\Delta G$ and electronically excited $C_{60}$ acceptor states for ET, could not exclude either explanation of the quenching mechanism.

TA measurements

As mentioned above, the $C_{60}^{\bullet-}$ radical anion absorption was beyond the experiment’s upper wavelength limit and the goal of these experiments was therefore to identify the transients observed in the accessible probe wavelength region. The difference spectra of the measurements carried out in toluene show two spectrally overlapping processes occurring over two distinct time scales: one ultrafast and sub-ps and the other over a much longer period. The latter occurs within 1 ps.
and decays with a lifetime $\gg 1 \text{ ns}$ and shows a negative signal at the blue wavelength detection limit as well as a positive contribution from 490 nm to beyond the red wavelength detection limit with two maxima at 510 and 560 nm. Due to these spectra being mainly the result of the differences between the measurements of the mixture and ZnTPP itself, a negative signal implies a reduced absorption observed within the former compared to the latter. This could either be caused by stimulated emission or alternatively by the absence or reduction of an absorbing species in the measurement of the mixture. Stimulated emission can be excluded due to the wavelength region. A bleach of the $C_{60}$ ground state population in the mixture can also be excluded based on the measurements of $C_{60}$ in toluene shown in Figure 3.7a, as well as the wavelength region. This only leaves the reduction of an absorbing species. Comparison to the SAS of ZnTPP in toluene shown in Figure 3.3d strongly suggests the $S_1$ state. This is in strong agreement with the observation of its quenching within the mixture. The matching time profiles of the negative and positive signal contributions suggest that the latter is due to the product formed from the $S_1$ state. As EnT can be energetically excluded, the additional absorption is attributed to the ZnTPP$^{•+}$ radical cation formed by ET from $S_1$ formed via IC from $S_2$. The spectral profile is in agreement with previous studies [9].

The rise of the ultrafast component centred around 650 nm clearly provides the kinetic profile to be attributed to the product of the ZnTPP $S_2$ decay within the complex with $C_{60}$. Even though the excited state processes within the latter are evidently complex, a comparison of the transient spectra of $C_{60}$ shown in Figure 3.7a and the spectral profile of the ultrafast component do not suggest the latter to be a $C_{60}$ excited state produced by EnT from ZnTPP. The alternative interpretation of ET to form a CS state obviously requires its attribution to a radical ion species. As mentioned above, the typical $C_{60}^{•−}$ radical anion absorption lies much further towards the infrared and can therefore be excluded. The ultrafast
component’s spectral profile is however clearly very similar to that of the long-lived absorption bands attributed to the ZnTPP$^{\bullet+}$ radical cation formed upon ET from its $S_1$ state. The slightly increased amplitude could be related to the increased quenching parameter for $S_2$ compared to $S_1$, indicating an increased conversion to the CS state from the former. It has, however, to be considered that while the difference spectra result solely from ZnTPP:C$_{60}$ interactions, the latter are not necessarily represented by a single species, as only moderate binding allows for a range of intermolecular distances and conformations, which might not contribute equally to the measurement. The quantification therefore remains tentative. The observation of partial return to the ZnTPP $S_1$ state after $S_2$ quenching, and reports from other groups observing excess vibrational and possibly electronic excitation to be preserved over several ET steps [14–16], suggest a potentially similar scenario. It is likely that the initially formed CS state is excited in some manner, and branching of the decay processes caused by the overlap of multiple potential energy surfaces results in the non-quantitative conversion. This equally provides an explanation for the rapid decay, which could be due to some form of excited CS state decaying to a vibrationally excited ground state, and thereby bypassing the formation of a longer-lived relaxed CS state or CR to the ZnTPP $S_1$ state. There is no observable spectral shifting indicative of a vibrational relaxation during the ET processes within the difference spectra, although the Soret band bleach region, where this has been observed [15] is unfortunately below the accessible probe wavelength range.

The observation of an extremely long-lived species in the difference spectra produced from the measurements in PhCN shown in Figure 3.9c is in agreement with the stabilisation of CS states in polar solvents. It is difficult to distinguish whether it is solely formed directly from excitation of the ground state complex, or also during collisions during the long-lived ZnTPP $T_1$ state lifetime. However, the ultra-fast component centred around 660 nm, shown in its kinetic profile in Figure 3.9d,
points to a very similar conclusion as in the toluene mixtures, i.e. fast ET from the \( S_2 \) state to an excited CS state, followed by rapid charge recombination to a vibrationally excited ZnTPP ground state. The interpretation of rapid ET rather than EnT is further supported by the longer lifetime of the ultrafast component in PhCN compared to toluene, which is again in agreement with an increased CS state stabilisation in the more polar solvent. The effect of the solvent polarity on the CS state decay rate suggests that CR occurs in the normal region of ET.

3.3 Conclusion

The measurements performed do not allow the exclusion of the possibility of parallel EnT to \( C_{60} \) contributing to the quenching of the observed ZnTPP \( S_2 \) state fluorescence, and the simultaneous presence of not independently observable species prohibits exact quantification. Nonetheless, the performed TA measurements strongly suggest the ultrafast formation of an excited CS state at a rate close to the magnitude of molecular vibrations (\( ca. 10^{13} \) s\(^{-1} \)) to be the primary decay process in \( S_2 \)-excited untethered ZnTPP:\( C_{60} \) complexes in solution. This places the CS reaction in the barrierless region, while the increase of the CS state lifetime in the more polar solvent indicates the occurrence of CR in the normal region. ET from the ZnTPP \( S_2 \) state has been inferred several times from time-resolved fluorescence measurements, although there have only been limited reports of direct spectroscopic observation of the initially formed product species [14, 16]. The measurements presented here therefore add to this body of evidence and are the first for a loosely bound donor-acceptor complex. The partial population of \( S_1 \) upon CR and the observed decay kinetics add further support to the involvement of electronically or vibrationally excited CS state species affecting subsequent relaxation processes.

The relatively loose binding in the investigated system obviously limits its direct practical application, but the close proximity in the complexes is very similar to the
3. Untethered ZnTPP:C$_{60}$ complexes

conditions chromophores experience in bulk devices. The presented work therefore clearly underlines the importance of higher excited states and their potential to act as electron donors and potentially acceptors, thus contributing to the overall performance of organic photovoltaic or photocatalytic devices.
References


3. References


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Chapter 4

A covalent

ZnTPP-amino-substituted
naphthalene diimide dyad

The goal of the work presented in this chapter was to investigate the decay processes of a photoexcited, covalently linked ZnTPP-amino-substituted naphthalene diimide (ANDI) dyad in solution. This compound was synthesised by the group of Professor Steven J. Langford, Monash University. This molecule was synthesised with the objective of mimicking the photoinduced ET behaviour of natural photosynthetic RCs and provide a building block that could be used to assemble larger supramolecular constructs for artificial photosynthetic devices. The molecular structure of the individual model chromophores as well as the dyad are shown in Figure 4.1. The findings presented here resulted in a joint publication titled “Ultrafast electron transfer in a porphyrin-amino naphthalene diimide dyad” [1].

Numerous studies investigating photoinduced ET in covalently linked dyads and larger systems have aided the understanding of this process as well as confirmed theoretical predictions [2–6]. Understanding the subtleties of this process and relating molecular structure and properties to observed behaviour with the goal of
A covalent ZnTPP-amino-substituted naphthalene diimide dyad

Figure 4.1: Molecular structures of model compounds and dyad.

determining rational design principles remains however challenging. Even though the role of the redox properties and solvent environment are well established [7–9], and the influence of the linking bridge structure in mediating or limiting the ET efficiency has also been investigated [10–14], the kinetic behaviour of novel chromophore systems remains difficult to predict accurately. This is especially important with regard to the goal of increasing CS state lifetimes. While copying the natural system by coupling more than two chromophores to allow directional multi-step ET is a frequent approach [15–17], an increased understanding at the dyad level is obviously conducive to overall improvement.

RC mimics frequently employ porphyrins and derivatives of NDIs (cf. 1.3.1) and have repeatedly been shown to undergo photoinduced ET [3, 15, 18–25]. The recent interest in ET commencing from the ZnTPP $S_2$ state following excitation into its Soret band (cf. 1.4.7) [26–28] and its observation in ZnTPP:C$_{60}$ complexes as described in Chapter 3 suggested that this might also occur in the ZnTPP-ANDI dyad discussed here, and was therefore investigated.
4.1 Sample preparation

The detailed synthesis of the ZnTPP-ANDI dyad has been described elsewhere [1]. 100 μM solutions of either ZnTPP or ZnTPP-ANDI in both toluene and PhCN were prepared for the TA measurements. Small portions of these stock solutions were correspondingly diluted for steady-state and time-resolved fluorescence measurements due to the differing employed cuvette path lengths.

4.2 Results and discussion

4.2.1 Steady-state spectroscopy

The absorption spectra of ZnTPP, ANDI and the ZnTPP-ANDI dyad in toluene are presented in Figure 4.2. The absorption spectrum of the ZnTPP exhibits the typical strong Soret absorption band with a maximum at 431 nm and the two weaker Q-bands with maxima at 563 and 601 nm characteristic of metalloporphyrins. The ANDI absorption maximum at 525 nm, which is not present in unsubstituted NDIs, has been attributed to a charge transfer-type transition arising from the interaction of the electron-donating 2-amino substituent with the naphthalene π-conjugated core [29]. Figure 4.2 shows that the dyad absorption spectrum closely agrees with the sum of the spectra of the ZnTPP and ANDI components, indicating that there is little perturbation of the electronic states of the individual chromophores arising from the covalent attachment.

Steady-state fluorescence spectra measurements employed 550 nm (toluene) and 560 nm (PhCN) for porphyrin $S_1$ excitation and 415 nm (both solvents) for $S_2$ excitation. The latter wavelength was chosen to minimise absorption by the ANDI moiety. The fluorescence originating from the ZnTPP $S_1$ state occurs above 550 nm and has a lifetime of 1.9 ns in toluene. The weak fluorescence from the $S_2$ state is discernible following excitation into the Soret band with a maximum at 430 nm in
4. A covalent ZnTPP-amino-substituted naphthalene diimide dyad

Figure 4.2: Absorption spectra (molar absorption coefficient vs. wavelength) of ZnTPP (dashed purple), ZnTPP-ANDI (solid purple) and ANDI (dashed green, with $\epsilon \times 25$) recorded in toluene.

In both toluene and PhCN the porphyrin $S_1$ fluorescence is highly quenched in the dyads compared to ZnTPP. The quenching of this fluorescence is very similar for the excitation in both the Soret band and the Q bands (ca. 90%). This is an indication that the conversion of the initially populated $S_2$ state to $S_1$ is quantitative, even though the pathway is not discernible from these steady-state measurements. The residual fluorescence of the dyad has a very similar lifetime (ca. 1.9 ns as measured via TCSPC) to the unquenched ZnTPP and was assigned to a small amount of unlinked porphyrin remaining from the synthesis. The high quenching of the inherently low quantum yield ZnTPP $S_1$ fluorescence required TCSPC acquisition times of several hours to achieve sufficient count rates, and therefore incurred considerable sample degradation as evident from the decrease in fluorescence intensity. None of the measures to improve the count rate by minimising instrumental losses could compensate for this. The assignment of additional lifetime components besides that resembling untethered ZnTPP was prohibited by the quality of the collected data. Therefore a reliable estimate for the quenched $S_1$ decay time could not be obtained by TCSPC measurements. The $S_2$ fluorescence is also quenched to a very similar
high degree (ca. 90 %) in both toluene and PhCN. The deactivation pathway must therefore occur at a rate beyond that of the otherwise dominating pathway of IC to $S_1$, similar to the case observed in the ZnTPP:C$_{60}$ complexes.

**Electrochemical measurements**

To aid the interpretation of the TA spectra, the absorption spectrum of the electrochemically produced radical anion of the ANDI model compound was recorded in DCM by a previously described method [31]. Similar to TA measurements, the electrochemical reduction leads to the depletion of the neutral ground state species and the recorded spectra are hence a combination of the radical anion absorption and a negative ground state bleach. As the two components are spectrally distinct, the correction for the ground state bleach was straightforward and produced the pure absorption spectrum of the ANDI radical anion shown in Figure 4.3. It is very similar to those reported of both substituted and unsubstituted NDI radical anions [32, 33], and is dominated by an absorption maximum around 490 nm and smaller maxima around 620 and 815 nm.

![Figure 4.3: Normalised absorption spectrum of the electrochemically generated radical anion of the ANDI model compound recorded in DCM and corrected for the contribution of the ground state bleach.](image)
4.2.2 TA measurements

In unsubstituted NDIs spectral overlap considerations exclude the possibility of energy transfer from either $S_1$ or $S_2$. However, the additional charge-transfer type band of core-substituted derivatives opens up the possibility of energy transfer occurring from the porphyrin $S_2$ state. Similar to the case of this possibility in the ZnTPP:C$_{60}$ system, Förster-type EnT is unlikely due to the low oscillator strength of the ANDI in the spectral overlap region with $S_2$ fluorescence. This leaves either Dexter-type EnT or ET to the ANDI as the possibilities for the deactivation pathway causing the $S_2$ fluorescence quenching. The fluorescence quenching data indicates that the porphyrin $S_1$ state is the ultimate product of the $S_2$ deactivation. EnT from the excited ANDI to porphyrin or CR from a higher charge-separated state would result in formation of $S_1$. The former process would involve the ANDI excited state whereas the latter would involve radical cation and anion species as intermediates. Therefore the pathway should be discernible from the differing transient absorption features of these species.

Measurements in toluene

The TA measurements of ZnTPP in toluene used here as the comparison were discussed in the previous chapter (cf. 3.1.1). The main aspects relevant to this investigation are the $S_1$ absorption, which is most pronounced towards shorter wavelengths with a 1.9 ns lifetime, and the short-lived feature around 650 nm of the $S_2$ absorption with a ca. 1.4 ps lifetime.

The TA spectra of the dyad in toluene shown in Figure 4.4 display very fast kinetics that return almost to the baseline within ca. 100 ps. Several spectral features are discernible: a broad absorption ranging from at least 460 nm (the shorter wavelength detection limit for the experiment) to approximately 700 nm, decaying over several tens of ps, a very fast decaying component absorbing from 600 to 700 nm
and a feature located towards the longer wavelength detection limit showing a slow rise reaching maximum intensity after ca. 10 ps. Ground state bleaching is clearly visible at 550 nm and partially at 590 nm.

Figure 4.4: TA spectra of 100 µM ZnTPP-ANDI in toluene recorded up to 100 ps after 415 nm excitation.

Visual inspection can discern several kinetically differing components: a very rapidly rising and decaying component prominent at 650 nm reaching a maximum ca. 200 fs after \( \Delta t_0 \), a slightly delayed component absorbing strongly at 460 nm reaching a maximum after ca. 700 fs, a rise and decay most clearly discernible towards the longer wavelength limit with maximum intensity after ca. 11 ps, and finally a much longer-lived component appearing towards the shorter wavelength limit.

It is clear that there is extensive spectral overlap of various species and assigning one species to a particular wavelength region is difficult. A preliminary interpretation by comparison to the transient absorption spectra of ZnTPP measured in the same solvent suggests a strong contribution of the porphyrin \( S_1 \) state to the TA features of the dyad from 460–600 nm. The broad absorption rising and decay-
ing over tens of ps, most obvious in the long wavelength region, is in agreement with the features reported for the ZnTPP radical cation [34]. The small peak above the absorption plateau at 490 nm matches the absorption maximum of the electrochemically produced radical anion of the ANDI model compound (cf. Figure 4.3). Even though strong absorption features at early times have considerably decayed within 100 ps, the ground state bleach indicates that these have not decayed fully to $S_0$. A scan up to 900 ps shows little change in the transient absorptions observed at 100 ps. These features match those of the $T_1$ of ZnTPP observed in toluene (cf. Figure 3.3d). Due to operating in aerated solutions its decay is shortened $<10$ µs (the pulse separation at the laser source RR) and was not investigated further.

The TA decay profiles recorded at various wavelengths are shown in Figures 4.5a&b. The very short-lived feature observed in the 650 nm decay profile (Figure 4.5b) is assigned to be the product of ET from the porphyrin $S_2$ state to form an excited CS state, CS’, which then decays rapidly by charge recombination to form the porphyrin $S_1$ state. This is similar to the observations made in similar ZnTPP-NDI dyads [26, 28] and the ZnTPP:C$_{60}$ complexes. A coherent artefact can be excluded from being responsible for this feature as no such feature is observed in the measurements of ZnTPP or neat toluene. While the $S_2$ absorption occurs over a similar wavelength region, the minimum quenching rate indicated by the steady-state fluorescence quenching ($\gtrsim 4 \times 10^{12}$ s$^{-1}$) indicates that any contribution by this component would be minor.

The decay profile at 650 nm shown in Figure 4.5b displays a fast decay within the first few ps, which is followed by a much slower rise and subsequent decay. The dominant contribution at this wavelength is expected to be due to the absorption of the ZnTPP$^{\bullet+}$ radical cation. The decay profile hence can be assigned to the rapid formation, fast decay and then subsequent re-formation and much slower decay.
4.2. Results and discussion

Figure 4.5: (a) Kinetic traces at selected wavelengths of the TA spectra of 100 µM ZnTPP-ANDI in toluene excited at 415 nm including lines of best fit as estimated by the hybrid GTA (cf. 2.5); (b) enlarged trace at 650 nm showing fast kinetics at early times.

of ZnTPP$^{•+}$. This behaviour is consistent with the repopulation of the $S_1$ state by charge recombination following the formation of a CS species via ET after $S_2$ excitation. Finally, the transient temporal behaviour indicates the close energetic proximity of the final CS state to the lowest porphyrin triplet state, and the latter is therefore the major end-product of the CS state decay, rather than the porphyrin $S_0$ ground state.

With these observations as the basis, the decay processes taking place following photoexcitation of the dyad are shown schematically in Figure 4.6 and this kinetic model was employed for the developed hybrid GTA to extract the rate constants of the various spectrally overlapped species. The rate constant for IC from $S_2$ to $S_1$ was fixed to the value measured for ZnTPP ($5.17 \times 10^{11}$ s$^{-1}$) and the rate constant for $S_2$-$S_0$ fluorescence ($8.7 \times 10^8$ s$^{-1}$) was fixed to a previously reported value [35], although the latter has little effect on the fitting due to the much lower magnitude. The assumption that these parameters remain unchanged from the symmetric donor model to the asymmetrically substituted donor within the dyad is obviously questionable. Ideally the corresponding values from a more appropriate model, e.g.
4. A covalent ZnTPP-amino-substituted naphthalene diimide dyad

a singly amino-substituted ZnTPP, would be employed, but such a compound was unfortunately not available. The small amount of substitution-induced perturbation of the ZnTPP excited states, as indicated from the comparison of the steady-state absorption spectra, nonetheless suggests that this assumption is valid to a sufficient extent.

Figure 4.6: Kinetic scheme employed in the hybrid GTA of the TA spectra of the ZnTPP-ANDI dyad.

The rate constant for ET from the porphyrin $S_2$ state to ANDI to form the initial $CS'$ state was fixed at the minimum value derived from the fluorescence quenching. This assumes that the rate of the main competing pathway of IC from $S_2$ to $S_1$ in the dyad is similar to that in ZnTPP. The magnitude of this rate constant ($\gtrsim 4 \times 10^{12}$ s$^{-1}$) limited the possibility of experimentally resolving this any further using the current instrumentation. All other rate constants shown in Figure 4.6 were allowed to vary freely during the fit optimisation. The rate constants for $S_1$ fluorescence, ISC from the porphyrin $S_1$ to $T_1$ and the $T_1$ decay to $S_0$ were omitted, since their magnitudes are far below those incorporated in the fitting and have hence very little effect on the fit quality.
Measurements in PhCN

The TA spectra of the dyad in PhCN shown in Figure 4.7 display very fast decaying kinetics compared to the model ZnTPP compound (cf. 3.1.2). A broad transient absorption across the entire probe spectrum employed with a maximum intensity near 600 nm is overlaid by the ground state bleaching of the porphyrin at 560 and 610 nm. Visual inspection of the decay profiles shows two overlapping kinetic species that can be assigned to the ZnTPP \( S_1 \) state absorbing from at least 460 to 700 nm and the porphyrin radical cation absorbing mostly above 550 nm and most apparent at the long wavelength detection limit. The differing rise times can be seen in the kinetic decay profiles shown in Figure 4.8. The marked differences compared to the measurements in toluene are the much faster rise and decay times, the absence of long-lived (> 100 ps) species and the absence of any observed components preceding the porphyrin \( S_1 \) state population. However, comparison to the TA spectra of ZnTPP in PhCN (cf. 3.1.2) shows that the \( S_1 \) absorption has a much faster rise time in the dyad, and that therefore the conversion from the initially excited porphyrin \( S_2 \) state to \( S_1 \) must be accelerated compared to the IC rate observed in ZnTPP. Whether this occurs via a CS’ state is not directly discernible from these measurements. Nonetheless, given the increase in driving force for ET due to the more polar solvent PhCN this is highly likely. A very small absorption of the ANDI radical anion at 490 nm is discernible but not as apparent as observed in toluene.

An interesting aspect, also observed in toluene, is a slight spectral blue shift of ca. 10 nm of the apparent ground state bleach minima at 560 and 610 nm over the scanned time range of 100 ps. The interpretation is again hindered by the extensive overlap of various species. The residuals of the best fit in the performed hybrid GTA, which assumes that the absorption spectrum of a species remains unchanged over time, indicates this is a real effect rather than a visual illusion caused by an
4. A covalent ZnTPP-amino-substituted naphthalene diimide dyad

Figure 4.7: TA spectra of 100 µM ZnTPP-ANDI in PhCN recorded up to 100 ps after 415 nm excitation.

Figure 4.8: Kinetic traces at selected wavelengths of the TA spectra of 100 µM ZnTPP-ANDI in PhCN excited at 415 nm including lines of best fit as estimated by the hybrid GTA.
4.2. Results and discussion

<table>
<thead>
<tr>
<th>Solvent</th>
<th>$k_{IC}$</th>
<th>$k_{fluor(S2)}$</th>
<th>$k'_{CS}$</th>
<th>$k'_{relaz}$</th>
<th>$k'_{CR}$</th>
<th>$k_{CS}$</th>
<th>$k_{ISC/CR}$</th>
<th>$k_{CR}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Toluene</td>
<td>51.7 (ZnTPP)</td>
<td>0.09 [35]</td>
<td>$\gtrsim 400$</td>
<td>&lt; 100</td>
<td>ca. 300–400</td>
<td>19.8</td>
<td>3.46</td>
<td>0.8</td>
</tr>
<tr>
<td>PhCN</td>
<td>n/a</td>
<td>0.09 [35]</td>
<td>$\gtrsim 400$</td>
<td>Unobservable</td>
<td>$k_{S2\rightarrow S1}$ ca. 400</td>
<td>80.4</td>
<td>n/a</td>
<td>15.9</td>
</tr>
</tbody>
</table>

Table 4.1: Rate constants derived from the hybrid GTA of the TA spectra for ZnTPP-ANDI excited at 415 nm in toluene and PhCN (in units of $10^{10}$ s$^{-1}$, values fixed during fitting procedure are shown in italics).

An overlap of kinetically differing species. A blue shift of this magnitude might be assigned to the relaxation of a vibrationally excited species, most likely the porphyrin $S_0$ state, and this is discussed further below.

The absence of a discernible CS’ state feature does not allow a realistic fit of its decay rate to the porphyrin $S_1$ state. The very similar $S_2$ fluorescence quenching observed in PhCN compared to toluene however hints at an equally similar rate of ET from $S_2$. The rapid formation of $S_1$ suggests that the rate of CR from the CS’ is faster than the formation rate of the latter, thereby not producing an observable quantity of any intermediate species. This considered, the effective rate constant encompassing the direct (IC) and indirect (CS followed by CR) pathways from $S_2$ to $S_1$ was fixed, for the purpose of the data analysis, at the assumed dominant yet rate limiting step of ET from $S_2$, hence $4 \times 10^{12}$ s$^{-1}$. The rate constants obtained from the fitting procedure for the various processes depicted in Figure 4.6 are summarised in Table 4.1.

An obvious extension to this work would be TA measurements following $S_1$ excitation, however there was insufficient pump pulse energy in this wavelength region using the present laser source and could not be pursued further during this project.

4.2.3 Electronic structure calculations

To gain insight into the localisation of the molecular frontier orbitals within this system, DFT calculations (cf. 2.6) were performed on isolated ANDI derivatives.
4. A covalent ZnTPP-amino-substituted naphthalene diimide dyad

The HOMO and LUMO density distributions of the ANDI model compound with partially truncated side-chains are shown in Figure 4.9. The same calculations were also performed on the same model appended with a phenyl moiety resembling the linking structure of the dyad and the accordingly altered HOMO and LUMO density distributions are shown in Figure 4.10. Their relevance is discussed below.

Figure 4.9: Density distributions of the frontier molecular orbitals of a partially truncated ANDI model as calculated by DFT methods at the B3LYP/6-31G(dp) level of theory: (a) HOMO; (b) LUMO.

4.2.4 Interpretation

ET occurring from the porphyrin $S_2$ to form a higher CS state ($CS'$), which then recombines to form the $S_1$ state that subsequently undergoes another ET step to form a further thermal CS state, has been reported in a similarly closely linked ZnTPP-NDI dyad in polar solvents [28]. The difference in the system investigated here is both structural and energetic. Rather than directly linking from the porphyrin meso-position to the imide nitrogen, the linkage in this system is via the core-substituent amino-group. As the frontier orbitals of the ANDI extend onto this group (cf. 4.2.3) it provides closer orbital overlap to the porphyrin frontier
4.2. Results and discussion

orbitals compared to linking to the imide nitrogen in the same way. This is however balanced by the interjecting phenyl moiety, so the overall coupling is likely to be similar. At the same time the core-substitution alters the energetic properties of the NDI, which in this case opens the complicating aspect of possible energy transfer from the porphyrin $S_2$ state. The TA measurements however indicate that electron transfer, rather than energy transfer processes from this state to the intermediate $CS'$ state and then the porphyrin $S_1$ state, are the dominant processes.

The observed solvent dependencies of the kinetics are in accord with the frequently encountered observation of $CS$ occurring in the Marcus normal region and $CR$ in the inverted region, in this case both for $ET$ from $S_1$ and $S_2$. The Rehm-Weller free energy changes upon $CS$ calculated from (1.3) are favourable in both solvents for both excitation to $S_2$ and $S_1$ ($\Delta G = -0.4$ electronvolt(eV) in toluene and $-1.2$ eV in PhCN for $S_1$ excitation). This is on the assumption of the $ET$ occurring in the non-adiabatic regime, which especially for proceeding from $S_2$ might not be true. Due to the increased stabilisation of the $CS$ state in polar

![Figure 4.10](image-url): Density distributions of the frontier molecular orbitals of a partially truncated ANDI model appended with a phenyl moiety as calculated by DFT methods at the B3LYP/6-31G(dp) level of theory: (a) HOMO; (b) LUMO.
solvents the rate of charge separation is expected to be faster than in non-polar solvents. Equally the lowering of the CS state should increase the rate of CR if it occurs in the Marcus inverted region. This is clearly the case for the charge separation and recombination steps originating from the porphyrin $S_1$ state in this dyad.

With the same assumptions being employed, the increased lowering of the CS’ state in the more polar solvent should result in equally faster charge separation originating from $S_2$ and faster charge recombination to populate the $S_1$ state. Although the CS’ state is not observed in PhCN, this can be explained by the increased rate of CR occurring beyond the time resolution of the experiment, considering it is already close to the limit in toluene. Whereas the TA measurements in PhCN do not allow the unambiguous exclusion of the possibility of two EnT steps starting from $S_2$ to yield $S_1$, the observation of a CS state intermediate in the less polar solvent toluene strongly indicates the same pathway will operate in PhCN.

The solvent polarity dependence of the CR rate is opposite to what is observed in the ZnTPP:C$_{60}$ complexes, where the initial CS state is longer-lived in PhCN compared to toluene (cf. 3.2.3). The nature and hence energetics of the initial CS’ state are in both cases not precisely known. The difference of ca. 0.1 eV in calculated $\Delta G$ values for ET from the ZnTPP $S_2$ state to either C$_{60}$ or ANDI is small. Not including the term accounting for the solvent environment in the Rehm-Weller equation (1.3) results in a similarly small difference of ca. 0.3 eV. This reversal might therefore be attributed to a smaller change in nuclear coordinates going from the $S_2$ to the CS’ state in the ZnTPP-ANDI dyad compared to the ZnTPP:C$_{60}$ complexes. This would shift CR from the normal to the inverted region and explain the inversion of the CR rate dependence on solvent polarity.

Given that the chromophore separation is small in both cases, and that the
acceptor is either above ($C_{60}$) or beside (ANDI) the ZnTPP plane, the orbital overlap cannot be quantified simply by a centre-to-centre measure. Where the differing extent of nuclear coordinate change would come from is therefore difficult to compare, but a tentative suggestion is that the dyad is closer to the ideal ET configuration in its ground state and hence requires less conformational changes once it is transferred to its excited state. If one considers that CS originating from the $S_2$ state is occurring at rate constants approaching $10^{13}$ s$^{-1}$ in both cases, the activation energy $\Delta G^\#$ must be close to zero, and hence indicates the barrierless region of ET according to Marcus theory [4]. A smaller separation of the nuclear coordinates between the local ZnTPP and the CS' states could also explain why the ANDI dyad returns to the $S_1$ rather than the $S_0$ ground state or a thermalised CS state. Semi-quantitative diagrams of the potential energy surfaces of the locally excited ZnTPP and CS' states of the $C_{60}$ complex and the ANDI dyad as well as the discussed areas of their intersections are shown in Figure 4.11.

Despite the close linkage of the two chromophores and the possibility of resonance structures involving the conjugated series of bonds stretching from the porphyrin core to the NDI core, the absence of stronger interaction can be explained by the torsional angle of the linking phenyl group. It is known that the phenyl groups in tetraphenyl porphyrins are tilted out of the plane of the pyrrole rings, due to the repulsion of the hydrogen atoms ortho to the phenyl-to-porphyrin meso-bond and the closest porphyrin $\beta$-hydrogens [36]. In the dyad studied in this work a very similar situation can be assumed. In core-substituted amino-naphthalene diimides the hydrogen bond from the amino-group to the imide carbonyl restricts rotation about the NDI to amine bond [29]. In this case however there would be repulsion between the hydrogen adjacent to the amino-group on the naphthalene core and the phenyl hydrogen ortho to the amine bond similar to the repulsion involving the porphyrin $\beta$-hydrogen. Even though the conformation of the dyad in solution
is unknown, it appears highly likely that the three planes described by the phenyl linker, the porphyrin pyrrole rings and the NDI’s naphthalene core are sterically prevented from assuming a coplanar conformation despite several degrees of freedom being available to the non-rigid linker. This is in agreement with the low ground state coupling observed. Theoretical calculations (cf. Figures 4.9 and 4.10) of the molecular orbitals of the core-substituted NDI clearly show partial localisation of the frontier orbitals on the amino-group, which considering its electrochemical effects is to be expected. The calculations additionally including the phenyl linker show that the frontier orbitals can extend onto the latter to an extent depending on the overall conformation. As the precise conformation in solution is not known, an accurate account of the extension of the frontier orbitals of the core-substituted NDI moiety onto the phenyl-linker is limited. The close proximity of frontier orbitals nonetheless provides an explanation for the high coupling between the two chromophores.

Figure 4.11: Schematic diagram of suggested potential energy surfaces for ET from $S_2$ in ZnTPP-ANDI and ZnTPP:C$_{60}$. The localised ZnTPP states are $S_0$ (black), $S_1$ (green) and $S_2$ (purple). The CS’ states formed upon ET from $S_2$ to the linked ANDI in toluene (red) or PhCN (magenta) or alternatively to the complexed C$_{60}$ in toluene (dashed red) or PhCN (dashed magenta) are in close energetic proximity. The vertical lines indicate the reaction coordinate of selected surface minima: the ZnTPP $S_2$ state (purple) as well as the CS’ states in the ANDI dyad (red) and the C$_{60}$ complex (dashed red). The surface intersections of the $S_2$ and CS’ states (purple boxes), the $S_1$ and ANDI dyad CS’ states (green box) as well as of the $S_0$, $S_1$ and the C$_{60}$ complex CS’ states (black box) are highlighted.
required for ET to compete with IC from the ZnTPP $S_2$ state. The motif of having a link between two chromophores that provides a high excited-state coupling and only a low ground state coupling could be useful in the design of molecular systems in which a more precise tuning of electronic coupling is required to favour a certain desired ET pathway.

ET from porphyrin $S_2$ states as an intermediate step after triplet-triplet annihilation has received increased interest with its relevance to solar energy conversion [37]. The objective is to produce a high-energy product rather than wasting photon energy in internal conversion. The investigated dyad shows that given the relative longevity of the $S_2$ state this step can occur with quantitative yield given the right combination of donor, acceptor, link and solvent. Charge recombination from the high-energy $CS'$ state to the $S_1$ state would however defeat this purpose and therefore needs to be addressed. One approach would be to employ a secondary acceptor. In both natural photosynthesis and other artificial systems spatially separating the electron further from the initial donor suppresses CR. Considering the encountered rates of the latter process, the secondary acceptor would have to be highly coupled to the initial acceptor for the additional charge separation process to be competitive. Energetics adjustable by both solvent polarity and the tunable redox properties of core-substituted NDI chromophores, and the possibility of high coupling to the latter by covalent attachment to the naphthalene core, could potentially make such a process viable. The single core substitution of the ANDI employed in this dyad is rather rare compared to the double substitution of many reported NDI derivatives [33], which could provide a synthetic avenue to a highly coupled triad.

An issue that could not be resolved was whether the $CS'$ state is vibrationally or electronically excited with respect to the $CS$ state. It is known that the porphyrin $S_1$ carries vibrational excitation after its formation from $S_2$ via IC, which it then
dissipates on a ps time scale [38]. Considering the small contribution of IC this is not likely to be the source of the observed vibrational cooling of the dyad. Hammarström et al. observed excess vibrational energy passing on through consecutive CS and CR events in a Zn(II) porphyrin-viologen complex from both \( S_2 \)- and \( S_1 \)-excited initial states into the \( S_0 \) ground state [27]. In the similar dyad investigated by their group the CS’ state is ascribed as being vibrationally excited with respect to the CS state [28]. Whilst it was not possible to provide further insight into the nature of the excitation of the CS’ state, the measurements appear to combine the elements of the two systems mentioned above: the double CS and CR decay pathway following \( S_2 \) excitation, and at least some of the excess vibrational energy of the excited states being dissipated through this pathway into the ground state.

### 4.3 Conclusion

In this investigation further evidence for ultrafast ET originating from the ZnTPP \( S_2 \) state has been demonstrated. The rapid charge recombination following \( S_2 \) excitation that re-forms the \( S_1 \) state is clearly a pathway that has to be addressed, if the charge separation from \( S_2 \) is to be effectively utilised in a process such as triplet-triplet annihilation/ up-conversion approaches of solar energy conversion. A further electron acceptor is required to extract the transferred electron from the primary acceptor if wasteful return to \( S_1 \) is to be avoided. The adaptive properties of core-substituted NDIs might allow for the design of a molecular triad similar to the systems achieving increased CS state lifetimes by utilising a secondary acceptor for ET originating in \( S_1 \) while reducing the energy loss usually incurred from the required electrochemical gradient. The utilisation of ultrafast ET steps would minimise energy losses due to thermal relaxation.

Ultrafast behaviour was not the initial expectation when this dyad was newly synthesised just prior to the commencement of this project. CS frequently occurs in
the normal and CR in the inverted region (cf. 1.4.1). It has therefore been a matter of debate whether increasing the electronic coupling $V_{DA}$, for example by a smaller donor-acceptor separation and hence greater orbital overlap, could accelerate the former and decelerate the latter, and thereby prolong the CS state lifetime without using the multi-step ET approach mentioned above [39–44]. A strong coupling can also be conducive to extending the lifetime of triplet CS states (cf. 1.4.3) [13, 44]. Given the small separation of the two chromophores there was some possibility that this system might display a prolonged CS state lifetime on the ns to µs time scale due to either inverted region or spin-selective effects. Ultrafast dynamics occurring on the time scale of the ps-lifetime of the ZnTPP $S_2$ state were therefore not part of the initially presumed behaviour. The findings presented here suggest that even if the condition of a high electronic coupling between dyad chromophores is met, ultrafast processes and non-thermally relaxed intermediates can clearly suppress long CS state lifetimes. As the latter is only one parameter affecting the efficiency of an artificial photosynthetic system, this nonetheless does not represent an obstacle, but rather an opportunity.
References


4. References


4. References


Chapter 5

Supramolecular ZnTPP:NDI complexes

The goal of the work presented in this chapter was to investigate the ET behaviour of photoexcited, self-assembled ZnTPP:NDI complexes in solution. The NDI derivatives employed were dipyridine naphthalene diimide (pyrNDI), diquinoline naphthalene diimide (quinNDI) and diisoquinoline naphthalene diimide (isoquinNDI). These bear identical N-donor substituents directly bonded to both of the imide nitrogens for the purpose of axial ligation to ZnTPP. As comparison models the acetamide-substituted derivatives of the linking moiety N-(4-pyridinyl)-acetamide (pyrMOD), N-(5-quinolinyl)-acetamide (quinMOD) and N-(5-isoquinolinyl)-acetamide (isoquinMOD) were used. These compounds were synthesised by the group of Professor Steven J. Langford, Monash University. The synthesis and characterisation of these compounds have been described elsewhere [1–3]. Their molecular structures are shown in Figure 5.1.

As discussed in 1.3.3, supramolecular assembly of RC mimics reduces synthetic requirements and thereby allows for potentially much larger and more complex molecular constructs [4–6]. This is evidently the chromophore assembly method the natural photosynthetic system has evolved to use [7, 8]. A number of studies of
5. Supramolecular ZnTPP:NDI complexes

(a) pyrMOD
(b) quinMOD
(c) isoquinMOD
(d) pyrNDI
(e) quinNDI
(f) isoquinNDI

Figure 5.1: Molecular structures of model compounds (a–c) and di-N-substituted NDI (d–f).

Supramolecular assemblies have employed derivatives of NDI [9–18] or the closely related pyromellitic diimide [19, 20] and PDI [21] as the acceptor for ET from photoexcited metal porphyrins. Synthetic accessibility, suitably matched redox potentials as well as the knowledge of the spectral profiles of their respective radical ion forms have been the main reasons for their frequent pairing [22–24]. Several studies have employed hydrogen bonding to form dyads from appropriately functionalised porphyrins and NDI [9, 13, 16, 18].

A synthetically simpler approach is to utilise axial coordination to the metal centre, for which especially zinc(II) porphyrins have proven popular. Complexation to porphyrin forces zinc(II) to adopt a $sp^2d$-configuration rather than the usually
preferred $sp^3$- or $sp^2d^2$-hybridisation [25]. The thus electron deficient $4p_z$- and $4d_{z^2}$-orbitals form $\sigma$-type coordination bonds with electron donor ligands. The closed shell of this ion does not permit dative metal to ligand $\pi$-bonds [26]. The coordination of an axial base forces the metal cation ca. 0.2–0.3Å out of the porphyrin plane towards the ligand, thereby resulting in a square-pyramidal symmetry and affecting the orbital energetics [27]. The ligand’s basicity is the dominant parameter affecting the strength of the metal-ligand interaction. In the absence of steric effects greater basicity typically results in stronger coordination to the metal centre and an accordingly higher binding constant [25, 27, 28]. While zinc(II) porphyrins form complexes most easily with nitrogen bases, coordination to oxygen or sulfur ligands is also feasible, albeit weaker [26, 29]. Enthalpy is the dominant contribution towards the free energy change of binding, and is typically an order of magnitude higher for nitrogen rather than oxygen based ligands, which results in accordingly greater binding constants [28]. The previously reported investigation of ligand exchange of ZnTPP coordinated by pyridine in solution showed “on”-rates in the order of $10^8 \text{M}^{-1}\text{s}^{-1}$ and “off”-rates in the order of $10^{4-5} \text{M}^{-1}\text{s}^{-1}$, which indicates kinetically labile complexation [30].

Despite several reports of N-donors other than pyridine displaying similar or even stronger binding to zinc(II) porphyrins compared to the latter [25, 28, 31, 32], none of these appear to have been used as the coordinating moiety in supramolecular RC mimics. Even if the binding strength and selectivity provided by pyridine were to be sufficient for a desired supramolecular architecture, additional binding motifs might offer increased modification capabilities and potentially allow for selective binding when used in conjunction with each other. The exploration of such alternatives was the motivation behind the study of the here investigated quinNDI and isoquinNDI coordination complexes with ZnTPP.
While there have been several reports of photoinduced ET between zinc(II) porphyrins and NDI derivatives axially ligated to the metal centre via a pyridine moiety [10–12, 14, 17], some ambiguity remains with regard to the decay pathways following the initial excitation. Investigations of both hydrogen bonded and axially coordinated supramolecular zinc(II) porphyrin:NDI complexes photoexcited to the former’s $S_1$ state have typically reported CS rate constants in the order of $10^9 - 10^{10}$ s$^{-1}$ [9–14, 16–18]. This is sufficient to compete with ISC to the donor’s $T_1$ state and results in a high quantum yield of the CS state. The reported CR rate constants are typically an order of magnitude smaller than those for CS, hence $10^8 - 10^9$ s$^{-1}$. This is consistent with fast, spin-allowed CR to reform the porphyrin $S_0$ ground state. There have however been reports of considerably longer-lived CS states. Work carried out within our research group showed the occurrence of such a long-lived state upon excitation of ZnTPP axially coordinated by pyridine, which in turn was covalently bound to the NDI by an ethylene linker, in non-polar solvents [14]. The observed rate constants of CR in the order of $10^6$ s$^{-1}$ were attributed to a triplet CS state. As described in 1.4.3, the return to the ground state is in this case formally spin forbidden and has to overcome very low interstate electronic coupling, which therefore drastically slows CR compared to a singlet CS state. Relatively slow CS from $S_1$ allowing for a sizeable ZnTPP $T_1$ state formation and subsequent ET from the latter were determined to be the decay processes leading to the observed behaviour. As sub-ns-TA measurements were not available at the time, the question of whether this long-lived CS state is solely formed via ET from $T_1$, or at least partially via ISC from the singlet CS state, could not be resolved. In conjunction with this study, the here investigated ZnTPP:pyrNDI complex, which has the pyridine moieties directly linked to the NDI imide nitrogens, thereby omitting the ethylene spacer, showed rapid CS beyond the time resolution attainable by TCSPC and no long-lived transients. Fukuzumi et al. studied a similar complex, which differs from ZnTPP:pyrNDI by the imide nitrogen, which is not linked to
the porphyrin coordinating pyridine moiety, carrying a hexyl chain rather than a second pyridine group [12, 17]. In PhCN rapid ET from $S_1$ was inferred from the latter’s reduction in lifetime. Additionally, a very long-lived CS state, which is understood to be the direct product of the former decay process, was observed with a CR rate constant in the order of $10^3$ s$^{-1}$. In non-polar benzene only the $T_1$ state was observed as a long-lived transient. Given the similarity between the two systems it is likely that the decay pathways are equally similar. The differences in the interpretation would be resolved by determining the decay kinetics of the initial product of the ZnTPP $S_1$ decay.

A further aspect is whether direct ET from the ZnTPP $S_2$ state to the NDI acceptor can occur in the three supramolecular complexes investigated here. As discussed in the previous chapters, Mataga et al. have observed this in a closely and covalently linked zinc(II) porphyrin-NDI dyad [33] while Harada et al. have observed this in a pyridine-coordinated pyromellitic diimide:ZnTPP complex [19]. The similarity between these and the systems investigated here indicate that this might be feasible.

### 5.1 Complex geometries

The predicted geometries of the three investigated ZnTPP:NDI complexes are shown in Figure 5.2. They were derived by combining the results of nuclear magnetic resonance (NMR) [34], crystallographic [14, 35], spectroscopic [24, 36, 37] and theoretical studies [21, 35, 38] presented in the literature.

As described above, ZnTPP only coordinates to a single N-donor and this complexation forces the metal ion above the porphyrin plane [14, 27, 35]. While the two coordinating moieties of the NDIs in principle allow the coordination to two separate metal centres, this has been shown to require mM-concentrations of ZnTPP [14, 37],
which were not employed during this investigation. Abraham et al. have reported on the complex structures of ZnTPP coordinated by pyridine, quinoline and isoquinoline studied by NMR methods [34]. The reported geometries for pyridine and isoquinoline are very similar, showing values of 2.5 Å and 2.4 Å respectively for the zinc-nitrogen coordination bond, and a 90° angle between the latter and the porphyrin plane. The steric repulsion between the hydrogen at the 8-position of quinoline and the porphyrin both increases the zinc-nitrogen separation to 2.8 Å and forces the coordinating moiety to adopt a geometry tilted by ca. 6° compared to pyridine and isoquinoline. This causes the axis described by the imide nitrogens of quinNDI to be tilted relative to the central normal of the porphyrin plane and, due to the linkage via the 5-position of quinoline, to be additionally offset relative to the porphyrin centre. The same axis in the complex with pyrNDI is identical to the porphyrin’s central normal. The linkage via the 5-position of isoquinoline results in a ca. 30° angle between the NDI imide nitrogen axis and the porphyrin plane in the complex with isoquinNDI.

If the aromatic system of the NDI core were able to combine with the equally aromatic coordinating substituents by adopting a coplanar arrangement, there would be a favourable energetic contribution. However, it has been shown that despite this, NDI aryl substituents adopt a perpendicular minimum energy confirmation [21, 24, 36, 38] similar to the case of the orientation of the porphyrin’s phenyl substituents [39]. In the case of pyrNDI and quinNDI changes in this dihedral angle have little or no impact on the orientation of the NDI core relative to the porphyrin plane. In the ZnTPP:isoquinNDI this would result in a more, although still tilted, edge-to-face rather than face-to-face relative orientation.

As stated above, the depicted geometries were constructed by combining the results of previously described studies. Further geometry optimisation was not per-
5.1. Complex geometries

![Predicted structures of 1:1 complexes of ZnTPP with the here investigated NDI derivatives.](image)

Figure 5.2: Predicted structures of 1:1 complexes of ZnTPP with the here investigated NDI derivatives.

<table>
<thead>
<tr>
<th>Complex with ZnTPP:</th>
<th>$d_{Zn-N}$(Å) [34]</th>
<th>ZnTPP∠NDI(°)</th>
<th>$R_{cc}$(Å)</th>
<th>$R_{ee}$(Å)</th>
</tr>
</thead>
<tbody>
<tr>
<td>pyrMOD</td>
<td>2.5</td>
<td>90</td>
<td>3.9</td>
<td>4.4</td>
</tr>
<tr>
<td>pyrNDI</td>
<td>2.5</td>
<td>90</td>
<td>10.2</td>
<td>7.1</td>
</tr>
<tr>
<td>quinMOD</td>
<td>2.8</td>
<td>84</td>
<td>4.4</td>
<td>7.8</td>
</tr>
<tr>
<td>quinNDI</td>
<td>2.8</td>
<td>84</td>
<td>10.9</td>
<td>7.8</td>
</tr>
<tr>
<td>isoquinMOD</td>
<td>2.4</td>
<td>30</td>
<td>5.0</td>
<td>7.8</td>
</tr>
<tr>
<td>isoquinNDI</td>
<td>2.4</td>
<td>30</td>
<td>10.3</td>
<td>7.8</td>
</tr>
</tbody>
</table>

Table 5.1: Predicted geometry parameters of 1:1 complexes of ZnTPP with pyrMOD, pyrNDI, quinMOD, quinNDI, isoquinMOD and isoquinNDI ($d_{Zn-N}$: bond distance between zinc(II) centre and coordinating nitrogen; ZnTPP∠NDI: angle between the normals of the respective molecular planes; $R_{cc}$ and $R_{ee}$: centre-to-centre and edge-to-edge distances).

formed, as isolated gas phase calculations without inclusion of the surrounding (aromatic) solvent environment are unlikely to achieve a more accurate description of the actual confirmation found in solution. A selection of the complexes’ geometry parameters including those used subsequently in the calculations of the driving force of photoinduced ET are given in Table 5.1.
5.2 Driving forces for photoinduced ET

To calculate the driving forces for ET from ZnTPP to the model or the NDI compounds in the respective complexes and solvents employed, the Rehm-Weller equation (1.3) was extended by the correction term (5.1b), which takes into account the ion solvation energy [40]:

\[
\Delta G = e \times [E_{Ox}(D) - E_{Red}(A)] - E_{00}
\]

\[
\frac{e^2}{4\pi\varepsilon_0\varepsilon_S R_{cc}}
\]

\[
-\frac{e^2}{8\pi\varepsilon_0} \left( \frac{1}{r_D} - \frac{1}{r_A} \right) \left( \frac{1}{\varepsilon_{ref}} - \frac{1}{\varepsilon_S} \right)
\]

where \(r_D\) and \(r_A\) are the ionic radii of the donor and acceptor, and \(\varepsilon_{ref}\) is the dielectric constant of the solvent in which the electrochemical parameters of the isolated donor and acceptor molecules were recorded.

Coordination of an N-donor to ZnTPP results in a small donation of electron density and accordingly a small stabilisation towards oxidation. Seely et al. [41] have reported on the half-wave potentials of the first one-electron oxidation of ZnTPP in the presence of various anions. For measurements in DCM they have reported values ranging from 0.50 to 0.89 V (all values here and in the following are given vs. the saturated calomel electrode (SCE)). With the non-coordinating perchlorate as the anion the oxidation potential is reported as 0.80 V, while in the additional presence of coordinating pyridine it is slightly lowered to 0.77 V. The latter value was chosen as \(E_{Ox}(D)\) due to the close resemblance of this system with the complexes investigated here [31]. As values for \(E_{00}\) for ZnTPP \(S_2^-\) and \(S_1\)-excitation 2.90 and 2.06 eV were employed, which are based on the intersection of the normalised absorption and emission spectra of the respective the electronic
states [31, 42]. Walters et al. [43] have reported the pyridine-coordinated ZnTPP T₁ phosphorescence as having a maximum at 789 nm. The value of E₀₀ for possible ET originating from T₁ is accordingly estimated to be 1.57 eV.

The reduction potentials for unsubstituted pyridine, quinoline and isoquinoline in DCM have been reported as −2.76, −2.18 and −2.22 V respectively [44]. Methyl-substitution at the 4-position of pyridine lowers the latter’s reduction potential by 0.1 V due to the small electron donating effect of the substituent. The Hammett σ-parameters for para-substitution are very similar for methyl and acetamide groups (−0.17 and −0.15 respectively) [45]. The reduction potential of pyrMOD is hence estimated as −2.86 V. The electron withdrawing effect of an acetamide substituent is offset by its mesomeric effect at the pyridine para-position, which results in the overall inductive effect similar to methyl-substitution. At the meta-position the mesomeric effect is weakened. Here an acetamide substituent is overall as electron withdrawing as a methyl group is electron donating with Hammett σ-parameters of +0.07 and −0.07 respectively.

The reduction potentials of various singly methyl-substituted quinolines are reported as −2.19 to −2.31 V [44]. EPR measurements of the pyridine, quinoline and isoquinoline radical anions show the highest spin density to reside on the 4-position of both pyridine and quinoline and the 8-position of isoquinoline [46]. The spin densities at the 5-position of quinoline and isoquinoline are approximately half the respective maximum value. Charton et al. [47] have reported that for both 5-substituted quinolines as well as isoquinolines the meta Hammett σ-parameters are the most appropriate. The acetamide substitution in quinMOD and isoquinMOD is accordingly expected to slightly increase their reduction potentials compared to their parent compounds. Due to not being located at the position of the highest spin density as in the case of pyrMOD, the magnitude of change is accordingly
expected to be smaller (< 0.1 V), and the reduction potentials of quinMOD and isoquinMOD are taken to be those of their parent compounds.

Non-substituted NDI bonded to a single hydrogen at each of its imide nitrogens has a reduction potential of $-0.58$ V in DCM [23]. While core substitution allows tuning this value over a wide range from at least $-1.33$ to $+0.60$ V [48, 49], terminal substituents have only a minor effect [23, 50]. NDIs carrying substituents which do not possess a mesomeric effect, e.g. linear or branched alkyl chains, typically have reduction potentials very close to those of the parent compound at ca. $-0.6$ V [14, 22, 23]. Directly bound aromatic substituents can aid the stabilising of the radical anion’s charge by permitting partial delocalisation when they are tilted towards the NDI plane. This lowers the reduction potential to ca. $-0.4$ to $-0.5$ V [14, 24, 51, 52]. The steric repulsion above discussed between the NDI carbonyl groups and the aryl substituent’s ortho-hydrogens prevents a fully coplanar geometry, which limits the extent of this stabilisation.

The first reduction potential of pyrNDI has been reported as $-0.42$ V in DCM [14]. While the quinoline and isoquinoline substituents allow for potentially greater delocalisation compared to the pyridine group, they are sterically bulkier. These two properties are likely to be closely balanced and for the following calculations the first reduction potentials of quinNDI and isoquinNDI are taken to be equal to the pyrNDI value. The values of the free energy change upon photoinduced ET calculated by (5.1) for the systems here investigated are provided in Table 5.2. The ionic radii of the ZnTPP donor and the NDI acceptors are taken to be 5 Å and 3.5 Å respectively [53]. The ionic radii of the model compounds were estimated as half their maximum diameter, hence 2.5 Å for pyrMOD and 3.6 Å for quinMOD and isoquinMOD. The standard values of solvent dielectric constants employed in the calculations were $\epsilon_S = 2.38$ for toluene, $\epsilon_S = 25.9$ for PhCN and $\epsilon_{ref} = 8.93$ for
Table 5.2: Calculated free energy changes for photoinduced ET in the complexes of ZnTPP with pyrMOD, pyrNDI, quinMOD, quinNDI, isoquinMOD and isoquinNDI in the solvents toluene and PhCN. Values given in italics are calculated from (5.1); non-italics include the correction terms (5.1a) and (5.1b). All values given in eV.

<table>
<thead>
<tr>
<th>ZnTPP:</th>
<th>Toluene</th>
<th></th>
<th>PhCN</th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>$S_2$</td>
<td>$S_1$</td>
<td>$T_1$</td>
<td>$S_2$</td>
</tr>
<tr>
<td>pyrMOD</td>
<td>0.73</td>
<td>1.57</td>
<td>2.06</td>
<td>0.73</td>
</tr>
<tr>
<td></td>
<td>0.51</td>
<td>1.35</td>
<td>1.84</td>
<td>0.27</td>
</tr>
<tr>
<td>pyrNDI</td>
<td>$-1.71$</td>
<td>$-0.87$</td>
<td>$-0.38$</td>
<td>$-1.71$</td>
</tr>
<tr>
<td></td>
<td>$-1.22$</td>
<td>$-0.38$</td>
<td>0.11</td>
<td>$-2.02$</td>
</tr>
<tr>
<td>quinMOD</td>
<td>0.05</td>
<td>0.89</td>
<td>1.38</td>
<td>0.05</td>
</tr>
<tr>
<td></td>
<td>$-0.28$</td>
<td>0.56</td>
<td>1.05</td>
<td>$-0.33$</td>
</tr>
<tr>
<td>quinNDI</td>
<td>$-1.71$</td>
<td>$-0.87$</td>
<td>$-0.38$</td>
<td>$-1.71$</td>
</tr>
<tr>
<td></td>
<td>$-1.19$</td>
<td>$-0.35$</td>
<td>0.14</td>
<td>$-2.02$</td>
</tr>
<tr>
<td>isoquinMOD</td>
<td>0.09</td>
<td>0.93</td>
<td>1.42</td>
<td>0.09</td>
</tr>
<tr>
<td></td>
<td>$-0.07$</td>
<td>0.77</td>
<td>1.26</td>
<td>$-0.27$</td>
</tr>
<tr>
<td>isoquinNDI</td>
<td>$-1.71$</td>
<td>$-0.87$</td>
<td>$-0.38$</td>
<td>$-1.71$</td>
</tr>
<tr>
<td></td>
<td>$-1.22$</td>
<td>$-0.38$</td>
<td>0.11</td>
<td>$-2.02$</td>
</tr>
</tbody>
</table>

DCM. Values for the free energy change are calculated by (5.1) with and without the terms accounting for the Coulombic work (5.1a) and (5.1b), to illustrate their respective contributions.

Due to the assumptions of equal redox potentials and ionic radii and the very similar values derived for $R_{cc}$, the calculated values for the free energy change in the NDI complexes are very similar. It is clear that photoinduced ET is energetically feasible from both the ZnTPP $S_1$ and $S_2$ states as well as in both toluene and PhCN within all NDI complexes. ET from the $T_1$ state is clearly energetically feasible in PhCN, while the driving force for this process in toluene is weak at best. ET from the ZnTPP $S_1$ state in these complexes in toluene is only moderately favourable
compared to PhCN. ET to pyrMOD can be excluded in all cases, while for quinMOD and isoquinMOD ET from the ZnTPP $S_2$ state might be feasible. Pyrazine has a very similar reduction potential to quinoline and isoquinoiline and has been shown to allow such a process to occur when complexed to ZnTPP [31]. In this case CR rapidly repopulates the donor’s $S_1$ state.

5.3 Steady-state spectroscopy

To investigate the questions of whether the proposed complexations occur and whether any of these introduce an additional decay process to the excited states of ZnTPP, steady-state spectroscopic measurements were performed. Solutions containing in all cases 5 µM ZnTPP as well as the respective complexing agent in concentrations ranging from 10 to 900 µM corresponding to a 2 – 180× excess were prepared for this purpose. The absorption spectra as well as emission spectra utilising varied excitation wavelengths were recorded for each of these.

5.3.1 Absorption measurements

As discussed above, axial ligation to the porphyrin metal centre alters the orbital symmetry and energetics and as a consequence induces a red-shift of both the Soret and the Q bands as well as altering the latter’s relative intensities [27, 28]. The extent of the red-shift is typically related to the $pK_a$ of the ligand, unless steric hindrance in the vicinity of the lone pair impedes coordination [26, 28, 29]. While toluene does not interfere with complexation [25, 32], PhCN competes for coordination to the porphyrin metal centre and values for the association constant $K_a$ are accordingly lowered [54, 55]. Coordination of amides to ZnTPP is feasible, yet considerably weaker than complexation by unhindered aromatic nitrogen bases [56], and is therefore unlikely to occur in a significant fraction of the complexes with the model compounds here investigated.
Hosmane and Liebman have discussed the $pK_a$ values of the conjugate acid forms of pyridine (5.17), quinoline (4.85) and isoquinoline (5.46) [57]. The greater basicity of isoquinoline compared to pyridine can be attributed to the former’s greater ability to stabilise additional charge by delocalisation. Although this should equally apply for quinoline and the latter’s gas phase basicity is indeed very similar to isoquinoline, steric hindrance of the hydrogen peri to the quinoline nitrogen lowers the basicity in solution. Association constants for pyridine to zinc(II) porphyrins in solution are typically 3900 – 6900 M$^{-1}$ [25, 27, 28, 32]. Electron donation by the substituent increases the $pK_a$ of 4-methyl-pyridine to 6.02 and accordingly increases its association constant with ZnTPP by a factor of ca. 1.5 [29]. The association constant for quinoline to ZnTPP has been reported as 16900 M$^{-1}$ [25, 26] with a spectral red-shift $> 10$ nm in chloroform [29]. The corresponding value for isoquinoline is, to the best of my knowledge, unreported in the literature. Imai and Kyuno have however reported on the association constants of pyridine and isoquinoline to a series of so-called picket fence zinc(II) porphyrins, and shown that the values for isoquinoline are increased by a factor of 1.3 – 2.3 compared to pyridine [32].

Based on the above information complexation would be expected for all the ligands here investigated. The $K_a$ values for pyrMOD would be expected to be similar to 4-methyl-pyridine, while due to the small electron withdrawing effect of the acetamide group at the 5-position the values for quinMOD and isoquinMOD would be expected to be decreased compared to their parent compounds. Due to the double substitution with N-donor moieties of the NDIs their $K_a$ values would be expected to be accordingly increased compared to their respective model compounds.

The absorption spectra recorded in toluene and PhCN are shown in Figures 5.3 and 5.4 respectively. The clearest evidence for complexation is provided by the series of absorption spectra of ZnTPP recorded in toluene and in the presence of
increasing quantities of pyrMOD shown in Figure 5.3a. At the highest concentration of added ligand the Soret and Q bands are shifted by 6 and 11 nm respectively and there are clear isosbestic points at 407, 426, 556 and 587 nm. The spectra recorded in the presence of pyrNDI display similar, albeit significantly smaller red-shifts. Neither quinMOD nor quinNDI appear to alter the porphyrin absorption. At the highest concentration of added isoquinMOD the Soret and Q bands are shifted by 3 and 5 nm respectively, while for isoquinNDI these shifts are 2 and 3 nm. The measurements carried out in PhCN display a similar behaviour to those acquired in toluene. Red-shifts are clearly discernible for the series with pyrMOD, isoquinMOD and isoquinNDI, while they are absent in those of quinMOD and quinNDI. The spectra acquired with the addition of pyrNDI are red-shifted to a smaller degree than those recorded in toluene, but additionally display a reduction in both the Soret and Q band intensities.

Despite the above stated expectations, it appears that in all but the case of pyrMOD only a fraction of ZnTPP, at most moderate, is axially complexed even at a high excess of added ligand. The two most likely causes for this are a weak binding strength and self-aggregation. The former would be caused by a reduction in the availability of the coordinating lone pair, which in turn could be the result of additional steric hindrance or an electron withdrawal from the aromatic system. Steric hindrance appears unlikely as there are no additional groups introduced in the vicinity of the coordinating nitrogen compared to the parent compounds pyridine, quinoline and isoquinoline.

Delocalisation of electron density from the aromatic ring system towards the acetamide or the NDI moiety could be the cause of this. Self-aggregation of ZnTPP is not significant at the employed low concentration in these solvents [58]. Mitra et al. have reported on the self-aggregation of quinolines and isoquinolines in solution [59],
5.3. Steady-state spectroscopy

- (a) Ligand: pyrMOD
- (b) Ligand: pyrNDI
- (c) Ligand: quinMOD
- (d) Ligand: quinNDI
- (e) Ligand: isoquinMOD
- (f) Ligand: isoquinNDI

Figure 5.3: Absorption spectra of 5 µM ZnTPP in toluene with ligand concentrations of 0 (blue) and ca. 10, 25, 50, 100, 250, 500 and 900 (red) µM. Q band region shown ×5.
5. Supramolecular ZnTPP:NDI complexes

(a) Ligand: pyrMOD
(b) Ligand: pyrNDI
(c) Ligand: quinMOD
(d) Ligand: quinNDI
(e) Ligand: isoquinMOD
(f) Ligand: isoquinNDI

Figure 5.4: Absorption spectra of 5 µM ZnTPP in PhCN with ligand concentrations of 0 (blue) and ca. 10, 25, 50, 100, 250, 500 and 900 (red) µM. Q band region shown ×5.
yet their NMR-based measurements employed concentrations several orders of magnitude greater than the maximum utilised here. The possibility of self-aggregation of the model compounds was not investigated further. It is however worth noting that while pyridine and quinoline have low melting points (−42 °C and −15 °C respectively), pyrMOD and quinMOD are solid powders at room temperature, indicative of greater intermolecular attraction compared to their parent compounds. The isoquinMOD material is of a soft, waxy consistency at room temperature and appears to have a melting point close to that of isoquinoline (26 − 28 °C). Such behaviour could explain the evident absence of a ZnTPP absorption red-shift for addition of quinMOD as well as the smaller than expected shifts for isoquinMOD.

While the addition of quinNDI to ZnTPP results in an equally absent effect as its model compound, pyrNDI addition induces a small shift and isoquinNDI is close to matching the moderate effect of isoquinMOD. While the arguments for the possibility of a weak binding strength discussed above apply equally to the NDI s, self-aggregation is highly likely to contribute to the evidently limited extent of ZnTPP complexation. NDI s are known for their propensity to π-π-stack in solution, especially when substituted with aryl substituents [23, 60, 61]. The onset of significant aggregation for such NDI s has been reported to occur below 100 µM and to be more pronounced in low polarity solvents [62]. The broadening of the NDI absorption features in toluene compared to PhCN as shown in Figures 5.5a and 5.5b is evidence for this. NDI s are also known to form ground state complexes with aromatic solvents, which result in broad, excimer-like emission profiles. Similar profiles arise for aggregates, although these retain at least some resemblance to the mirror image of the absorption spectrum [63]. The fluorescence spectra of the here investigated NDI compounds shown in Figures 5.5c and 5.5d are therefore assigned to be the result of complexation with the aromatic solvents.
5. Supramolecular ZnTPP:NDI complexes

Figure 5.5: Model (pyrMOD, quinMOD and isoquinMOD: dashed blue, green and red) and NDI (pyrNDI, quinNDI and isoquinNDI: solid blue, green and red) absorption spectra and NDI derivative fluorescence spectra in toluene and PhCN.

To determine the association constant for a given ligand, the following equations [14] were used in conjunction with a non-linear least-squares regression analysis carried out in MATLAB:

\[
\Delta \epsilon = \frac{\Delta \epsilon \left( a - \sqrt{a^2 - 4K^2_a[ZnTPP]_T[Ligand]_T} \right)}{2K_a} 
\]

\[ a = 1 + K_a ([ZnTPP]_T + [Ligand]_T) \] (5.2a)

where the subscript \( T \) denotes the total solution concentration and \( \Delta \epsilon \) describes the change of the extinction coefficient between free and complexed ZnTPP at a chosen wavelength. Fitting (5.2) and (5.2a) to the absorption changes induced by
ligand addition of pyrMOD in either of the employed solvents as well as the addition of isoquinMOD in toluene allowed the determination of the respective association constants. In all other cases the magnitude of the spectral changes were either too small or overlapped with ligand absorption and could therefore not provide reliable values. The results of this fitting are shown in Figure 5.6.

The values of $K_a$ for complexation to ZnTPP for pyrMOD in toluene and PhCN were found to be ca. 3700 M$^{-1}$ and ca. 1600 M$^{-1}$ respectively, which is comparable to the values reported for pyridine [25, 27, 28, 32]. The reduced value in PhCN is in agreement with the solvent’s competitive binding mentioned above. The association constant for complexation of isoquinMOD to ZnTPP was calculated to be ca. 900 M$^{-1}$. The weaker binding for isoquinMOD compared to pyrMOD is likely to be due to the electron withdrawing effect of the former’s acetamide substituent.

Overall the absorption measurements suggest that the greatest extent of complexation with the model compounds occurs for pyrMOD and to a moderate extent with isoquinMOD. Compounds quinMOD and quinNDI do not appear to induce any ZnTPP spectral red-shifts and it therefore seems unlikely that axial ligation is occurring. The red-shifts induced by the addition of pyrNDI and isoquinNDI are
smaller than those induced by their respective model compounds, although in the case of the latter only to a small degree.

5.3.2 Fluorescence measurements

To investigate the occurrence of additional decay pathways for the excited states of ZnTPP in the presence of added ligand, the ZnTPP $S_2$ emission as well as $S_1$- and $S_2$-excited $S_1$ emission spectra were recorded for each added ligand concentration. The measurements carried out in toluene and PhCN are presented in Figures 5.7 and 5.8 respectively. Figures 5.7a–f as well as Figures 5.8a–f show the ZnTPP $S_2$ emission, Figures 5.7g–l as well as Figures 5.8g–l show the ZnTPP $S_2$-excited $S_1$ emission, and Figures 5.7m–r as well as Figures 5.8m–r show the ZnTPP $S_1$-excited $S_1$ emission.

$S_2$ fluorescence

The small Stokes shift of the ZnTPP $S_2$ emission requires excitation at the blue edge of the Soret band. The very small quantum yield for ZnTPP $S_2$-$S_0$ emission in the order of 1% [58] required the application of the procedure described in 2.2.2. The respective excitation wavelengths were set to the value of the complexation’s isosbestic point in this region. In cases in which an insufficient magnitude of induced red-shift or overlap with the ligand absorption prevented the determination of the exact position of an isosbestic point, the excitation wavelength was set to the estimated value of the latter. In all cases the value was kept identical for corresponding pairs of model and NDI compounds in the given solvent. In toluene the excitation wavelength was set to 407 nm in all cases. In PhCN it was set to 409 nm for the pyrMOD and pyrNDI measurements and to 405 nm for the remaining systems.

In toluene the ZnTPP $S_2$ emission undergoes a small red-shift and minor narrowing of the emission band with increased present concentrations of pyrMOD. The quantum yield relative to uncomplexed ZnTPP as calculated from the integrated
emission is unchanged within the limits set by the accuracy of the measurement. The observations for addition of pyrNDI to ZnTPP in the same solvent are very similar. The minor reduction in quantum yield is most certainly due to the competing absorption of the ligand. The measurements of the ZnTPP $S_2$ emission performed with increasing concentrations of quinMOD are overlapped by a weak yet obscuring fluorescence contribution attributable to the ligand itself. The apparent small red-shift of the $S_2$ emission peak is likely to be an artefact of this overlap. There appears to be no significant reduction in the quantum yield. The spectral series recorded in the increasing presence of quinNDI is similar to the one recorded for pyrNDI, showing a small quantum yield reduction most likely caused by the competitive absorption of the ligand. The apparent red-shift at high ligand concentration is unlikely to be caused by axial complexation given the absence of any spectral shift in the corresponding absorption measurements, and is also likely to be caused by a small fluorescence contribution from the ligand. The emission profile series recorded in the presence of isoquinMOD and isoquinNDI are similarly obscured by a fluorescence contribution attributable to the respective ligand. There is nonetheless a discernible reduction in the ZnTPP $S_2$ emission intensity. For isoquinNDI the competitive absorption of the ligand at the excitation wavelength is likely to be the dominant cause of this reduction and any further inference of an additional quenching process would be tentative. Given the minimal absorption of isoquinMOD and the very minor changes of the ZnTPP extinction coefficient upon complexation at the employed excitation wavelength, the reduction in $S_2$ emission intensity indicates the possibility of an additional decay pathway. As discussed in 5.2, ET from ZnTPP to this ligand appears energetically feasible and would lead to the observed quenching effect. The magnitude of quenching would be dependent on the rate of this process compared to that of the otherwise quantitative IC to the ZnTPP $S_1$ state. The possibility of such behaviour is discussed further below.
The $S_2$ emission profiles recorded with an increasing addition of pyrMOD in PhCN are similar to those in toluene, displaying a small red-shift, a minor narrowing of the emission band and an unaffected quantum yield. For all other series recorded in this solvent there is an increase in obscuring ligand fluorescence compared to the respective measurements in toluene. For all three NDI compounds, especially quinNDI and isoquinNDI, the nonetheless discernible reduction in ZnTPP $S_2$ emission intensity is likely to be mostly caused by the ligand’s competitive absorption at the excitation wavelength. Any inference of an additional quenching process would be tentative. For measurements utilising quinMOD and isoquinMOD as the ligand, competitive absorption at the excitation wavelength is however much lower. The strongly obscuring ligand fluorescence in the quinMOD series prevents the evaluation of any ZnTPP $S_2$ emission reduction. However, for the isoquinMOD series in PhCN a similar yet equally tentative interpretation to the one relating to the corresponding series in toluene can be made, i.e. the occurrence of an additional decay pathway upon complexation quenching the ZnTPP $S_2$ emission.

**Q band fluorescence**

The ZnTPP Q band fluorescence was recorded for both $S_2$- as well as $S_1$-excitation. CR following ET from a zinc(II) porphyrin $S_2$ state has in several cases been shown to populate the $S_1$ rather than the ground state, in which case there is little difference in the observed $S_1$ quenching following either the latter process or direct excitation [33, 53, 64–67]. Although the Q band fluorescence is in all cases shown as normalised such that the emission maximum of ZnTPP in the absence of any ligand is unity, excitation near the Soret band maximum obviously results in a stronger signal due to the higher extinction coefficient. Analogous to the $S_2$-$S_0$ emission measurements, the excitation was set either to the wavelength of a suitable isosbestic point in the absorption spectra series or alternatively to the wavelength of the Soret or Q band absorption maximum of uncomplexed ZnTPP. In all cases the value was
retained for the measurements of corresponding pairs of model and NDI in a given solvent. For the pyridine-based compounds the two excitation wavelengths were 426 and 556 nm in toluene and 430 and 560 nm in PhCN. For both the quinoline- and isoquinoline-based compounds these values were 423 and 550 nm in toluene and 429 and 565 nm in PhCN.

The ZnTPP \( S_1 \) emission profile series recorded with increasing concentrations of pyrMOD in toluene for both excitation wavelengths display a clear red-shift, isosbestic points and changes in the relative Q band intensities. The integrated emission intensities show no significant changes. Emission profiles recorded in the presence of pyrNDI in the same solvent are reduced by ca. 20\% at the highest employed ligand concentration. The absence of any red-shift in the recorded fluorescence indicates that it arises from uncomplexed ZnTPP, which therefore suggests that even at a high excess of ligand approximately 80\% remain unbound, and is in agreement with the observations made on the corresponding series of absorption spectra. The absence of an observable spectral shift also indicates that quenching in complexes is very high and hence occurs at a faster rate than the otherwise dominating rate of ISC to the ZnTPP \( T_1 \) state. The slightly increased degree of quenching for the Soret-compared to the Q-band-excited series can be attributed to competitive absorption by the ligand at the former’s excitation wavelength. Both series recorded for each of the quinoline-based ligands appear unaffected by the ligand concentration. This provides further evidence that neither ligand coordinates to ZnTPP, in line with the observations made for the corresponding series of absorption spectra. The emission profile of \( S_2 \)-excited ZnTPP in the presence of the maximum employed concentration of isoquinMOD in toluene resembles the analogue utilising pyrMOD, albeit at a much smaller concentration of the latter, in line with a correspondingly smaller value of \( K_a \). The emission profile series recorded in the presence of isoquinNDI in toluene display a similar behaviour to those recorded for pyrNDI. At the highest
employed concentration of ligand the emission intensity is reduced by \textit{ca.} 35%, but there is no observable spectral shift or change in the relative intensities. This once again suggests that the remaining fluorescence originates from uncomplexed ZnTPP and also that the complexed species is rapidly quenched and therefore does not contribute any shifted fluorescence to the overall emission profile.

Similar observations to those made in toluene can be seen in PhCN. The addition of pyrMOD induces a red-shift and changes in the relative intensities in the $S_1$-$S_0$ fluorescence profiles, although to a smaller degree. This is in accord with the smaller induced changes observed for the absorption spectra, in line with the competitive complexation of this solvent as discussed above. The emission series recorded in the presence of pyrNDI in PhCN equally display an analogous behaviour to toluene, showing a reduction in emission intensity without observable spectral changes. This is once again indicative of a high fraction of uncomplexed ZnTPP even at high ligand concentrations as well as rapid quenching of the $S_1$ emission in the complexed species. Analogous to the measurements in toluene, the presence of quinMOD induces no observable changes to the porphyrin emission profile. The small reduction in observed fluorescence intensity in the presence of quinNDI can be attributed to competitive absorption by this ligand. The spectral changes caused by isoquinMOD are similar, yet smaller compared to those observed in toluene. Both the $S_2$- and $S_1$-excited emission profile series recorded in the presence of isoquinNDI in PhCN once again show a reduction in the fluorescence intensity without notable spectral changes. This is indicative both of its origin being uncomplexed ZnTPP as well as the occurrence of rapid quenching of the $S_1$ state in the complexed species.
Figure 5.7: Fluorescence spectra of 5 μM ZnTPP in toluene with ligand concentrations of 0 (blue) and ca. 10, 25, 50, 100, 250, 500 and 900 (red) μM. Each series is scaled by a common factor setting the intensity maximum in absence of ligand to unity.
Figure 5.8: Fluorescence spectra of 5 µM ZnTPP in PhCN with ligand concentrations of 0 (blue) and ca. 10, 25, 50, 100, 250, 500 and 900 (red) µM. Each series is scaled by a common factor setting the intensity maximum in absence of ligand to unity.
5.3. Steady-state spectroscopy

Interpretation

Overall the steady-state experiments show that complexation does not occur to the extent envisaged. Only pyrMOD is capable of complexing a moderate to high fraction of ZnTPP in the employed solvents. While a low fraction is complexed by pyrNDI at a great excess of the latter, neither of the quinoline derivatives quinMOD and quinNDI appear to induce any complexation. However, the iso-quinoline derivatives isoquinMOD and isoquinNDI both afford a moderate extent of ZnTPP-complexation at the maximum employed concentrations.

The fluorescence measurements clearly show that the ZnTPP $S_1$ state only displays significant quenching when a NDI derivative is complexed to the metal centre, i.e. in the cases of pyrNDI and isoquinNDI while not in the case of quinNDI. Neither of the complexing model compounds pyrMOD and isoquinMOD appear to induce any additional decay pathways of the ZnTPP $S_1$ state. Combining these observations with the literature reports of similar systems discussed above, as well as the calculated driving forces, strongly suggests that photoinduced ET occurs in both ZnTPP:pyrNDI and ZnTPP:isoquinNDI complexes. In both these cases the quenching of the directly excited $S_1$ emission clearly indicates that ET to the NDI occurs from this state. Previous reports have shown that the ZnTPP $S_1$ lifetime is reduced to a small extent by complexation with pyridine derivatives [14, 20]. Assuming a similarly minor decrease in the complexes with pyrNDI and isoquinNDI and considering the high degree of quenching inferred for these complexes, it can be deduced that CS from the ZnTPP $S_1$ state must in both cases occur with a rate constant within close proximity of the $10^9 – 10^{10}$ s$^{-1}$ range reported for similar systems [9–14, 16–18]. This is investigated in the following section.

The fluorescence measurements do not reveal whether ZnTPP $S_2$ excitation is in all cases merely followed by IC to $S_1$, or if ET can occur directly from the
higher excited state in any of the formed complexes, especially for those in which this is calculated to be highly feasible energetically. Given the very short ZnTPP $S_2$ lifetime, the rate of CS would have to be at least in the order of $> 10^{11}$ s$^{-1}$ and occurring within the first few ps following photoexcitation. The possibility of such ultrafast behaviour is correspondingly investigated in the following section.

5.4 TA measurements

For the purpose of time-resolved measurements the developed TA set-up described in 2.4 was utilised. Sample solutions contained in all cases 100 µM ZnTPP and a tenfold excess of the respective model or NDI ligand. In all cases an excitation wavelength of 415 nm was employed. Even though the NDI compounds weakly absorb at this wavelength, the ZnTPP extinction coefficient in this region is in all cases at least 250× greater, so that more than 95% of the excitation intensity is captured by the latter, despite the tenfold excess of ligand. Q band excitation was not feasible as there was insufficient pump pulse energy in this wavelength region using the present laser source, and consequently could not be pursued further during this work.

As discussed above, numerous studies have documented photoinduced ET from ZnTPP to NDI derivatives. While the steady-state measurements carried out clearly predict a considerable contribution of unbound ZnTPP to the TA signal, the observed quenching equally indicates that any observed kinetic deviations caused by the introduction of an NDI ligand are highly likely to be due to ET behaviour. The investigation of such differences on the time scales of the typical ZnTPP $S_1$ and $S_2$ state lifetimes is presented in the following sections.

5.4.1 Time region up to 900 ps following excitation

The TA spectra recorded for ZnTPP in the presence of pyrMOD in toluene, which as discussed above achieves the highest degree of complexation of the here investigated
5.4. TA measurements

ligands, are shown in Figure 5.9. The high degree of complexation is evident from the 10 nm red-shift of the Q band bleach minima at 560 and 600 nm compared to those observed in the absence of ligand (cf. 3.1.1). The strong $S_1$ state absorption in the 500 to 600 nm region, the overlapping $T_1$ rise most noticeable at 480 nm and the short $S_2$ feature most discernible from 600 to 700 nm clearly show that the axial ligation by the N-donor only induces small changes to the photoexcited ZnTPP TA spectra.

Figure 5.9: TA spectra of 100 µM ZnTPP in the presence of 1 mM pyrMOD in toluene recorded up to 900 ps after 415 nm excitation.

The addition of pyrMOD leads to a high degree of complexation and the ki-
5. Supramolecular ZnTPP:NDI complexes

Figure 5.10: Kinetic profiles of the TA spectra of 100 µM ZnTPP in toluene up to 900 ps after 415 nm excitation in the presence of 1 mM of ligand. Lines shown as dashed for model compounds and solid for NDI derivatives. Intensities are normalised for the purpose of comparison.

Figure 5.10 shows the kinetic traces for the TA spectra of 100 µM ZnTPP in toluene up to 900 ps after 415 nm excitation in the presence of 1 mM of ligand. Lines shown as dashed for model compounds and solid for NDI derivatives. Intensities are normalised for the purpose of comparison.

For pyrNDI, the recorded traces are however dominated by the contribution of uncomplexed ZnTPP. Their comparison in the S1 state absorption region presented in Figure 5.10a shows a very similar, parallel decay at longer time delays, while there is an initial faster deactivation in the presence of pyrNDI occurring during the first few hundred ps. The trace for pyrNDI at 615 nm presented in Figure 5.10d shows a small yet discernible rise and subsequent decay over the same time scale.

The TA spectra recorded with quinMOD as the intended ligand show no discernible spectral or kinetic changes in accord with the absence of complexation evidence in the steady-state measurements. The spectra recorded in the presence of
quinNDI however display an additional contribution with a slow, continuous increase over several hundred ps with significant contributions at the wavelengths shown in Figure 5.10b&ce. Even though a small fraction of quinNDI is initially excited, the reported rapid rate of ISC from $S_1$ to $T_1$ on a ps time scale for terminally substituted NDI's [61] allows the exclusion of this component from being attributed to the latter.

The ZnTPP TA traces recorded in the presence of isoquinMOD and isoquinNDI, both of which afford at least a moderate extent of complexation, are presented in Figures 5.10c&f. While the former result in a very similar kinetic profile to free ZnTPP, those for isoquinNDI show a fast decay component in the $S_1$ state region within the first 200 ps, which is matched by a corresponding rise at 615 nm. Overlapping with this fast rise there is an additional, more slowly increasing contribution visible at both selected wavelengths similar to the behaviour seen for quinNDI.

The TA spectra of ZnTPP recorded in the presence of the investigated ligands in PhCN display similar behaviour and changes to those recorded in toluene. A significantly differing, additional observation is however made in the series of spectra recorded in the presence of the NDI ligands in this solvent. They all display clearly discernible, broad spectral features at delay times prior to $\Delta t_0$, which are shown in Figure 5.11. This was not observed with any of the measurements in toluene or those utilising the model compounds in PhCN. They are very similar to those encountered in the measurements of the ZnTPP:C$_{60}$ system in the same solvent discussed in 3.2.3. Following the same considerations, as well as the absence of such features in the measurement utilising the model compounds, these very long-lived transients are attributed to the ZnTPP radical cation. The assignment to a porphyrin species is supported by the evident Q band bleach contribution. With the latter taken into account, the underlying transient absorptions also clearly display greater absorptivity in the wavelength region above 600 nm compared to
the ZnTPP $T_1$ state (cf. Figure 3.6c). Further, yet more tentative confirmation of a CS state species comes from the small shoulder at 475 nm, which matches the maximum of the reported NDI radical anion absorption spectrum [22].

Figure 5.11: TA spectra of 100 $\mu$m ZnTPP in the presence of 1 mM pyrNDI (blue), quinNDI (green) or isoquinNDI (red) in PhCN recorded 5 ps prior to (equivalent to ca. 10 $\mu$s after) $\Delta t_0$ using 415 nm excitation.

Long-lived transients formed upon photoexcitation of ZnTPP in PhCN and in the presence of non-coordinating electron acceptors such as dipentyl-NDI [14] and fullerenes [69] have been reported previously. In both cases these transients are attributed to long-lived CS states formed by ET from the ZnTPP $T_1$ state and facilitated by the charge stabilisation of the polar solvent. Especially given the similarity to the former system the same conclusion can be drawn here. Given that these features are present more than 10 $\mu$s after the initial excitation and their decay rate has to be accordingly slow, it is reasonable to assume that the amplitude of their contribution to the TA signal is only minimally reduced over the scanned time range of the experiment. The pre-$\Delta t_0$ amplitudes were therefore subtracted from the corresponding sets of spectra for comparison of the kinetic profiles discussed below.
The second oxidation potential of ZnTPP is only ca. 0.3 V higher than the first [41] and oxidation of the radical cation to the dication accordingly requires a smaller driving force. The same applies to the reduction of a terminally substituted NDI radical anion, where the second reduction potential is lowered by ca. 0.4 V compared to the first [22]. However, based on the considerable reduction in the extinction coefficient at the employed excitation wavelength of the radical cation compared to the neutral form of ZnTPP [68], as well as the minimal overall concentration in the sample solution, the absorption contributions of products of a secondary photoinduced CS are likely to be negligible.

The kinetic profiles of the TA spectra of photoexcited ZnTPP in PhCN in the presence of model or NDI ligands are shown in Figure 5.12. The wavelength value selected for the comparison in Figures 5.12a–c is once again chosen due to the dominant ZnTPP $S_1$ state absorption in this region. The wavelength value employed for the comparison in Figures 5.12d–f is selected for the observation of the ZnTPP radical cation. Comparison of the kinetic traces of measurements employing pyrMOD and pyrNDI as the ligands are shown in Figures 5.12a&d. While the model compound does not appear to alter the kinetic behaviour of ZnTPP, the NDI analogue causes a relatively rapid initial decay in the $S_1$ state region accompanied by a rise and subsequent decay in the radical cation absorption region. Both are overlapped with a strong contribution from uncomplexed ZnTPP. From the near parallel decay at delay times beyond 500 ps in the traces at 550 nm, it can be estimated that approximately 15% of ZnTPP is complexed in accord with the observations made in the steady-state experiments.

Similar to the observation made in the spectra recorded in toluene, quinMOD does not induce any discernible changes to the features of ZnTPP recorded in PhCN,
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Figure 5.12: Kinetic profiles of the TA spectra of 100 \(\mu\)M ZnTPP in PhCN up to 900 ps after 415 nm excitation in the presence of 1 mM of ligand. Lines shown as dashed for model compounds and solid for NDI derivatives. Intensities are normalised for the purpose of comparison.

while in the presence of quinNDI an additional, slowly rising contribution is observable. The kinetic traces of the TA spectra utilising isoquinMOD and isoquinNDI as the intended ligands are shown in Figures 5.12c&f. Again a fast decay in the ZnTPP \(S_1\) state absorption region, with an accompanying rise and subsequent decay in the radical cation absorption region, is only observable for the isoquinNDI ligand.

Overall the observations made in the TA measurements confirm the conclusions drawn from the steady-state experiments: at least partial complexation occurs for the pyridine and isoquinoline derived ligands in both the employed solvents, but not for the quinoline derived ligands, and relatively rapid ET to a complexed NDI ligand depletes the ZnTPP \(S_1\) state to form a radical ion CS state. The observation of very
5.4. TA measurements

long-lived transients in PhCN with all three NDI ligands investigated here shows additionally that ET can also occur upon diffusional encounter during the extended ZnTPP $T_1$ state lifetime. The slowly rising contributions observed for quinNDI and isoquinNDI are likely to be evidence of this.

To extract the rate constants of CS state formation and CR in the encountered ZnTPP:NDI complexes, the kinetic traces at 615 nm of the TA spectra of ZnTPP recorded in the absence of any ligand were subtracted from those recorded with either pyrNDI or isoquinNDI. In all cases the subtracted trace was scaled to the maximum value that did not result in a negative difference value at the earliest delay times. The difference traces thus derived are shown in Figure 5.13. These profiles were fitted with the equation describing the time-dependent concentration of the intermediate between two consecutive first-order reactions:

$$I = \frac{k_{CS}}{k_{CR} - k_{CS}} \times \left( e^{-k_{CS}t} - e^{-k_{CR}t} \right) \times [C] \times c_I$$ (5.3)

where in this case $I$ is the observed, ZnTPP radical cation dominated absorption of the intermediate CS state, $k_{CS}$ and $k_{CR}$ are the respective rate constants for CS and subsequent CR, $[C]$ is the concentration of initially excited complexes and $c_I$ is a constant scaling factor accounting for the signal intensity of the CS state.

While the differences for pyrNDI as the ligand in toluene are small, the rate constant for CS can be nonetheless derived and is determined as ca. $4 \times 10^{10}$ s$^{-1}$. The evidently slow CR prevents the determination of an accurate value, but the fit shown in Figure 5.13a employs a value of $10^8$ s$^{-1}$ for $k_{CR}$, and a maximum upper limit of $10^9$ s$^{-1}$ can be derived. The difference trace for isoquinNDI as the ligand in toluene is shown in Figure 5.13b. While the initial fast rise can be fitted with the same value as the corresponding trace for pyrNDI in toluene, hence $k_{CS} = 4 \times 10^{10}$ s$^{-1}$, there is an evident, overlapping and much more slowly rising contribution, which
5. Supramolecular ZnTPP:NDI complexes

Figure 5.13: Kinetic profiles at 615 nm of the TA spectra of 100 µM ZnTPP after 415 nm excitation either in the presence of 1 mM of ligand (solid blue or red) or its absence (solid black). Intensities are normalised for the purpose of comparison. Points (blue or red) show derived differences (×5 for (a) only), cf. text for details. Dotted black lines show fits to (5.3).

prohibits reliable fitting of \( k_{CR} \). The maximum upper limit for the value of \( k_{CR} \) can be nonetheless derived as \( 10^9 \text{ s}^{-1} \).

In PhCN the differences are much more distinguishable. Fitting of (5.3) allows an accurate determination of the respective rate constants. For the difference traces derived from the measurements utilising pyrNDI as the intended ligand shown in Figure 5.13c, the values of \( k_{CS} \) and \( k_{CR} \) are determined as \( 6.0 \times 10^{10} \text{ s}^{-1} \) and \( 1.7 \times 10^{10} \text{ s}^{-1} \) respectively. For the difference traces derived from the measurements utilising isoquinNDI as the intended ligand shown in Figure 5.13d, the values of \( k_{CS} \) and \( k_{CR} \) are determined as \( 6.5 \times 10^{10} \text{ s}^{-1} \) and \( 0.7 \times 10^{10} \text{ s}^{-1} \) respectively. The numerical results of the fitting are summarised in Table 5.3.
5.4. TA measurements

<table>
<thead>
<tr>
<th>ZnTPP:</th>
<th>Toluene</th>
<th>PhCN</th>
</tr>
</thead>
<tbody>
<tr>
<td>pyrNDI</td>
<td>$k_{CS}$ 4 $&lt; 0.1$</td>
<td>6.0 1.7</td>
</tr>
<tr>
<td>isoquinNDI</td>
<td>ca. 4 $&lt; 0.1$</td>
<td>6.5 0.7</td>
</tr>
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Table 5.3: Values of rate constants for CS and CR in the investigated ZnTPP:NDI complexes derived from fitting with (5.3). All values given in $10^{10}$ s$^{-1}$.

The derived values are fully consistent with those reported for similar systems [10, 11, 14, 16]. The observation of both faster CS as well as faster CR in the higher polarity solvent is equally in agreement with the frequent observation of the former occurring in the normal and the latter occurring in the inverted region of ET [70–74]. The very similar values observed for pyrNDI and isoquinNDI also support the assumption discussed above that their respective reduction potentials are equally similar. The slightly greater donor-acceptor separation in the ZnTPP:isoquinNDI complexes (cf. Table 5.1) is likely to contribute to the small reduction in both the $k_{CS}$ and $k_{CR}$ values compared to the pyrNDI complexes. The latter is however equally consistent with a greater stabilisation of the CS state caused by the greater charge delocalisation capability of isoquinoline compared to pyridine moieties. Such a resonance effect would require these terminal substituents to rotate away at least partially from a perpendicular orientation and into the plane of the NDI core. The greater relative discrepancy between the two complexes for the rate of CR compared to the rate of CS might therefore be tentatively attributed to such a molecular motion, leading to a greater stabilisation of the NDI radical anion following, rather than prior to, the initial ET step.

5.4.2 Time region up to 20 ps following excitation

As described above, ET directly from the ZnTPP $S_2$ state has been reported for similar systems [19, 33]. The steady-state fluorescence experiments did not provide
clear evidence for additional decay pathways introduced by the complexation to any of the investigated ligands. The comparison of the $S_2$ decay and $S_1$ rise dynamics with those of the uncomplexed species should however allow this to be clarified. To this end, the kinetic traces recorded for delay times up to 20 ps after $\Delta t_0$ in both toluene and PhCN are shown in Figures 5.14 and 5.15.

Figure 5.14: Kinetic profiles of the TA spectra of 100 $\mu$M ZnTPP in toluene up to 20 ps after 415 nm excitation in the presence of 1 mM of ligand. Lines shown as dashed for model compounds and solid for NDI derivatives. Intensities are normalised for the purpose of comparison.

Figures 5.14a–c and 5.15a–c show the fast decay of the $S_2$ absorption feature while Figures 5.14d–f and 5.15d–f show the accompanying rise of the $S_1$ state [67]. For both the pyridine and quinoline derived ligands the observed profiles are indistinguishable from those recorded for ZnTPP in the absence of any ligand, displaying an $S_2$ lifetime of ca. 1.4 ps in both employed solvents. The same applies to the kinetic
5.4. TA measurements

(a) :pyrMOD & :pyrNDI, \( \lambda = 656 \text{ nm} \)

(b) :quinMOD & :quinNDI, \( \lambda = 656 \text{ nm} \)

(c) :isoquinMOD & :isoquinNDI, \( \lambda = 656 \text{ nm} \)

(d) :pyrMOD & :pyrNDI, \( \lambda = 540 \text{ nm} \)

(e) :quinMOD & :quinNDI, \( \lambda = 540 \text{ nm} \)

(f) :isoquinMOD & :isoquinNDI, \( \lambda = 540 \text{ nm} \)

Figure 5.15: Kinetic profiles of the TA spectra of 100 \( \mu \text{M} \) ZnTPP in PhCN up to 20 ps after 415 nm excitation in the presence of 1 mM of ligand. Lines shown as dashed for model compounds and solid for NDI derivatives. Intensities are normalised for the purpose of comparison.

Traces recorded in the presence of isoquinMOD. The only measurements displaying a significant deviation are those recorded utilising isoquinNDI as the intended ligand. In both toluene and PhCN the relative intensity of the initial \( S_2 \) absorption, as shown in Figures 5.14c and 5.15c, is lowered compared to the signal intensity at longer delay times. This observation is accompanied by the TA signal in the ZnTPP \( S_1 \) absorption region reaching its maximum intensity significantly earlier, as shown in Figures 5.14f and 5.15f.

Due to the very short ZnTPP \( S_2 \) state lifetime any additional decay pathway can only occur within complexes formed prior to excitation. While the differences are distinct, they are too closely associated with the IRF to allow an accurate
5. Supramolecular ZnTPP:NDI complexes

separation of the contributions arising from free and complexed ZnTPP. Given that no such changes are observed for pyrMOD, the compound achieving the greatest extent of complexation of the here investigated ligands, or similarly isoquinMOD, mere coordination by the isoquinNDI N-donor moiety can be excluded as the cause. EnT from ZnTPP can also be excluded on energetic and spectral grounds. This leaves ET as the only plausible option, but this opens up the question of the subsequent decay pathways. For similar dyad systems return to the ZnTPP $S_1$ state [31, 33, 53, 64, 66, 67], relaxation to a thermalised CS state [19] and combinations thereof [75] have been reported. Frequently an excited initial CS state is inferred [33, 76, 77]. The accelerated rise in the ZnTPP $S_1$ state absorption region strongly suggests that the necessarily rapid ET step depleting the $S_2$ state is followed by a similarly fast CR to $S_1$. As the thermalised CS state is evidently energetically below $S_1$, this has to involve an excited CS state. Partial relaxation to the thermalised CS state cannot be excluded. Given the considerable overlap of several different absorbing species on the time scale of the IRF, robust quantification of the associated rate constants is not feasible. However, the comparison of the measurements recorded in the two solvents suggests some acceleration of this decay pathway in PhCN compared to toluene. This solvent dependency of the kinetic behaviour is further indication of an ET process occurring.

Under close scrutiny similar yet significantly smaller deviations can be seen between the kinetic profiles recorded with pyrMOD and pyrNDI as the intended ligands in PhCN shown in Figures 5.15a&d. These differences allow not more than a tentative attribution of a similar pathway in ZnTPP:pyrNDI complexes. The values for $k_{CS}$ from the ZnTPP $S_1$ state are very similar for both the pyrNDI and isoquinNDI ligands. With an estimation from the respective ZnTPP radical cation signal intensities (cf. Figures 5.13c&d), the extent of complexation is approximately twice as great for isoquinNDI in PhCN. If the trends in the $S_1$ state ET behaviour for these
two ligands transferred to the $S_2$ state, greater deviations than those observed would be expected for pyrNDI, despite the lower extent of complexation. It can therefore be tentatively concluded that isoquinNDI has a greater propensity than pyrNDI to act as the acceptor for ET from the ZnTPP $S_2$ state. While such an ET process can be clearly excluded for both the complexing model compounds pyrMOD and isoquinMOD, the isoquinoline moiety’s frontier orbitals are positioned energetically much closer to the ZnTPP $S_2$ state (cf. 5.2), and might therefore facilitate donor-acceptor electronic coupling in the complexes formed with isoquinNDI.

5.5 Conclusion

The goal of the work presented in this chapter was to determine whether the investigated NDI derivatives are suitable building blocks for the construction of supramolecular RC mimics utilising ZnTPP as the donor for photoinduced ET. The successful assembly achieved with pyrNDI provides further confirmation of previous reports of pyridine being utilised as the coordinating moiety. The complexation and ET behaviour observed for the isoquinNDI ligand demonstrate the potential of N-donors other than pyridine as supramolecular construction tools. This obviously allows an extension of synthetic and hence structural approaches. More importantly, the effect of the isoquinNDI ligand on the ZnTPP $S_2$ decay behaviour strongly suggests that certain supramolecular binding motifs can provide more than a merely structural function. While the energetic properties of covalent linkages have been extensively studied, those of non-covalent means of assembly warrant further investigation.

The inability to form complexes with ZnTPP of the quinoline derivatives investigated here equally demonstrates that not all N-donor compounds are suitable supramolecular building blocks. Given that the parent compound binds to ZnTPP, the lack of sufficient binding strength is likely to be caused by the substituent.
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Altering the substitution position might allow the coordinating ability to be improved to a sufficient level. In order to achieve efficient assembly of supramolecular systems utilising NDI derivatives, a further issue that has to be overcome is their strong tendency towards aggregation. Given that synthetic capabilities have been extended to both terminal and core substituents, the addition of bulky groups to increase steric repulsion and minimisation of aromatic groups, i.e. the removal of one of the coordinating moieties, should allow this to be achieved.

The observed ET behaviour is in full accord with the expectations regarding a ZnTPP:NDI dyad with a short linkage. In the complexes the ZnTPP $S_1$ state rapidly undergoes efficient ET. The thus formed CS state decays over the time scale of hundreds of ps via CR to reform the ground state species. The observed solvent dependency of the ET kinetics shows that CS occurs in the normal, and CR in the inverted region. Uncomplexed photoexcited ZnTPP decays predominantly by ISC to its $T_1$ state, which can undergo ET to an NDI acceptor by diffusional encounter, not requiring prior complexation. The radical ion species thus formed display a µs-lifetime in the polar solvent PhCN. The magnitude observed for the rate constants of CS and subsequent CR following initial population of the ZnTPP $S_1$ state demonstrate clearly that the long-lived transients are not formed from the excitation of the complexes, but rather from the unbound donor species.

Finally, an additional decay pathway of the initially excited ZnTPP $S_2$ state in complexes with isoquinNDI is inferred from the TA measurements carried out in both employed solvents. Following the observations discussed above, this is interpreted as rapid ET to a non-thermalised CS state being followed by similarly rapid CR to the ZnTPP $S_1$ state in accord with previous studies. This behaviour is tentatively attributed to the involvement of the coordinating isoquinoline moiety’s frontier orbitals in the ET processes occurring.
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Chapter 6

An \textbf{NDI}_2-SnTPP:(OPh-BODIPY)_2 array

The goal of the work presented in this chapter was to investigate the photophysical behaviour of the chromophore array shown in Figure 6.1. It comprises a central tin(IV) tetraphenylporphyrin (SnTPP) covalently linked to two NDIs and axially coordinated by two phenolate moieties covalently each linked to a boron dipyrromethene (BODIPY). All the compounds discussed here were synthesised by the group of Professor Steven J. Langford, Monash University [1, 2].

Tin(IV) porphyrin complexes have been far less frequently studied compared to their zinc(II) analogues. Arnold and Blok have provided a comprehensive summary of their general properties [3]. Tin(IV) porphyrins are usually six-coordinate with two trans-diaxial and typically anionic ligands, and therefore provide a versatile building block for chromophore arrays. They are highly oxophilic and form stable complexes with carboxylate and aryloxide ligands. Due to the high metal charge they are easily reduced and difficult to oxidise. This is obviously inverted compared to zinc porphyrins. Their optical properties are however typical of porphyrins.

BODIPYs have been frequently used as sensitisers for porphyrins due to their ab-
Figure 6.1: Molecular structure of the \( \text{NDI}_2\text{-SnTPP}:(\text{OPh-BODIPY})_2 \) array.

absorption maximum being located between the typical Soret and Q bands ranges \([4]\). Besides this, their photostability and high fluorescence quantum yield have added to their appeal \([5]\). The idea of using BODIPY as a light harvesting antenna for subsequent EnT to a linked porphyrin has been employed numerous times \([5–11]\).

As mentioned in the previous chapters, NDIs have been extensively utilised as acceptors for photoinduced ET in porphyrin containing systems. To aid the study the model compounds shown in Figure 6.2 were also investigated. Beside the dihydroxy parent compound, \( \text{SnTPP}:(\text{OH})_2 \), this included the diphenolate derivative, \( \text{SnTPP}:(\text{OPh})_2 \), the phenolate linked BODIPY derivative \( \text{SnTPP}:(\text{OPh-BODIPY})_2 \), and the covalent \( \text{NDI}_2\text{-SnTPP}:(\text{OH})_2 \) triad.

During the course of this project Lazarides \textit{et al.} reported the study of the photophysical behaviour of the \( \text{SnTPP}:(\text{OPh-BODIPY})_2 \) chromophore system, which also included the investigation of the \( \text{SnTPP}:(\text{OPh})_2 \) and \( \text{SnTPP}:(\text{OH})_2 \) models \([12]\). In the \( \text{SnTPP}:(\text{OPh-BODIPY})_2 \) system excitation of a BODIPY chromophore leads to
Figure 6.2: Molecular structure of investigated model compounds.
fast EnT to the porphyrin centre, and accordingly to the population of the latter’s $S_1$ state. This state is rapidly quenched by ET from the phenolate moiety to the excited porphyrin and thereby forms the latter’s radical anion. The CS state thus formed undergoes CR to the ground state over tens of ps.

Although the phenolate was presumably intended as a linking moiety, such ET behaviour was first inferred from steady-state fluorescence quenching by Reddy and Maiya [13] and was also observed in several SnTPP:(OPh-NDI)$_2$ systems studied by our group [14]. In the latter system no ET to NDI was observed, yet a varying degree of phenolate induced quenching appeared to be modulated by conformational dynamics affected by the NDI substituents.

In the following the findings of Lazarides et al. [12] are briefly confirmed and the effect of the additional NDI moieties discussed. In the continuation of the investigation of the role of the porphyrin $S_2$ state in the previous chapters, this aspect is also examined further.

### 6.1 Results and discussion

The steady-state absorption and fluorescence spectra of all compounds investigated are shown in Figure 6.3. This includes the protonated, free ligand BODIPY-PhOH. The axial coordinated ligands as well as the covalently linked NDIs induce minor changes to the porphyrin absorption features, which in all cases show the intense Soret band as well as the lower intensity Q bands. The NDI-substituted porphyrin systems are slightly red-shifted. The BODIPY absorption is located between the Soret and Q bands both spectrally as well as in intensity, and appears unaffected by the inclusion in the overall array. The NDI extinction coefficients are significantly smaller (cf. Figures 5.5a and 4.2) than those of both SnTPP and BODIPY and therefore contribute only marginally to the spectral profiles of the systems in which
this moiety is included.

Figure 6.3: (a) & (b) Absorption spectra (molar absorption coefficient vs. wavelength) of the investigated array and model compounds (Q band region above 525 nm with \( \epsilon \times 10 \); SnTPP:(OH)\(_2\): solid black; SnTPP:(OPh)\(_2\): dashed black; SnTPP:(OPh-BODIPY)\(_2\): solid green; BODIPY-PhOH: dashed green; SnTPP:(OPh)\(_2\): dashed black; NDI\(_2\)-SnTPP:(OH)\(_2\): solid blue; NDI\(_2\)-SnTPP:(OPh-BODIPY)\(_2\): solid red). (c) & (d) The corresponding emission spectra for isoabsorbing (\( A_{405 \text{ nm}} = 0.15 \)) porphyrin solutions. The BODIPY-OPh absorption was optically matched to SnTPP:(OPh-BODIPY)\(_2\) at the former’s absorption maximum at 505 nm.

In SnTPP:(OH)\(_2\), SnTPP:(OPh)\(_2\) and SnTPP:(OPh-BODIPY)\(_2\) a small chlorin impurity is observed, but not in either of the NDI-substituted systems. It is discernible from the absorption feature at 625 nm and the central peak at 630 nm in the SnTPP(OH)\(_2\) emission spectra [15]. Maiti et al. have previously discussed the difficulty of removing chlorin impurities from tin(IV) porphyrin material [15].
They state that this is due to their tendency to be photochemically reformed in the presence of trace reductants, citing earlier work by Debaig-Valade et al. [16]. No further attempts were made to remove these impurities, as their extent did not interfere with the investigation of the target systems.

The SnTPP fluorescence is heavily quenched for all bar the solely NDI substituted system, which suggests rapid quenching of the porphyrin excited states. Beside the $S_1$ fluorescence, it is equally notable that the $S_2$ emission at 430 nm is heavily quenched as well. Considering the fact that the absorption spectra only show minor changes caused by the axial ligation, this indicates the possibility of additional decay pathways for the depopulation of $S_2$ other than IC to $S_1$. To investigate this further the TA spectra following SnTPP $S_2$ excitation were recorded in toluene and PhCN. For the purpose of time-resolved measurements the developed TA set-up described in 2.4 was utilised. Sample solutions contained in all cases 100 µM of the respective compound. In all cases an excitation wavelength of 415 nm was employed.

6.1.1 SnTPP:(OH)$_2$

The optical properties of SnTPP:(OH)$_2$ are very similar to those of ZnTPP. This similarity extends to their respective time-resolved profiles. The former’s TA spectra recorded in both toluene and PhCN are shown in Figure 6.4, including kinetic traces at selected wavelengths.

The initially excited $S_2$ state, which shows an absorption feature most discernible between 600 and 700 nm, undergoes rapid IC to $S_1$, which absorbs mostly between 500 and 600 nm. These absorption features are overlapped with the Q band bleach. The kinetic profiles showing the $S_2$ decay and accompanying $S_1$ rise are shown in Figures 6.4c&d. The $S_2$ lifetimes, which are predominantly determined by the rate of IC to $S_1$ [15], are ca. 1.3 ps in both employed solvents. These values are minimally
6.1. Results and discussion

(a) SnTPP:(OH)$_2$ in toluene
(b) SnTPP:(OH)$_2$ in PhCN

c) Kinetic profiles in toluene up to 20 ps after $\Delta t_0$
(d) Kinetic profiles in PhCN up to 20 ps after $\Delta t_0$

e) Kinetic profiles in toluene up to 900 ps after $\Delta t_0$
(f) Kinetic profiles in PhCN up to 900 ps after $\Delta t_0$

Figure 6.4: TA spectra of 100 $\mu$M SnTPP:(OH)$_2$ in toluene (a) and PhCN (b) recorded up to 900 ps after 415 nm excitation. Kinetic profiles at selected wavelengths in toluene (c)&(e) and PhCN (d)&(f).
shorter than those observed in ZnTPP or those reported for SnTPP:Cl$_2$ [15] in the same solvents (both ca. 1.4 ps). On a longer time scale the $S_1$ state undergoes ISC to $T_1$. The decay of $S_1$ and the corresponding rise of $T_1$, which is clearly discernible at 490 nm, are shown in Figures 6.4e&f. The observed $S_1$ lifetime of ca. 1.4 ns is in accord with previous reports [12, 15].

**6.1.2 NDI$_2$-SnTPP:(OH)$_2$**

As mentioned above, excitation of this array to the porphyrin $S_2$ state results in a ca. 50% quenched $S_2$ emission compared to the SnTPP:(OH)$_2$ parent compound in both employed solvents (cf. Figure 6.3c&d). However, following the same excitation the porphyrin $S_1$ emission appears unquenched in toluene, yet also ca. 50% quenched in PhCN. However, the corresponding fluorescence intensities following excitation to the porphyrin $S_1$ state shown in Figure 6.5 indicate at most minimal quenching compared to SnTPP:(OH)$_2$. These observations indicate an additional deactivation pathway of the porphyrin $S_2$ state, which eventually repopulates the $S_1$ state in toluene, yet not in PhCN. Such solvent-dependent behaviour is strongly indicative of ET. EnT from SnTPP to either of the NDI moieties can be excluded on energetic grounds.

As discussed in the previous chapters, ZnTPP has been frequently employed as the electron donor for photoinduced ET. There are however only limited reports of SnTPP adopting the role of the electron donor [17], which — given its known resistance to oxidation [3] — is unsurprising. To investigate this possibility further, the free energy changes for photoinduced ET from SnTPP to NDI were calculated from (5.1) with and without the additional correction terms (5.1a)&(5.1b). Lazarides et al. have reported a value of 1.56 V vs. SCE for the half-wave potential of the first one-electron oxidation of SnTPP:(OH)$_2$ in DCM [12]. They note that this oxidation was irreversible during their electrochemical measurements. For NDI's
6.1. Results and discussion

(a) Fluorescence in toluene, $\lambda_{ex} = 560$ nm

(b) Fluorescence in PhCN, $\lambda_{ex} = 560$ nm

Figure 6.5: Emission spectra of porphyrin $S_1$-excited and isoabsorbing ($A_{560\,\text{nm}} = 0.15$) solutions of SnTPP:(OH)$_2$ (black) and NDI$_2$-SnTPP:(OH)$_2$ (blue) recorded in toluene and PhCN.

with terminal alkyl substituents a corresponding reduction potential of $-0.61$ V vs. SCE in DCM has been reported [18]. These values were employed for $E_{Ox}(D)$ and $E_{Red}(A)$ respectively. The values of $E_{00}$ were derived from the intersection of the normalised absorption and emission spectra. For $S_2$ and $S_1$ excitation these were 2.89 and 2.09 eV in toluene and 2.88 and 2.08 eV in PhCN.

SnTPP typically adopts an octahedral geometry, in which the meso-linkages lie within the porphyrin plane and the phenyl groups are significantly rotated out of this plane [19], in very close similarity to ZnTPP [20]. If one considers the rigid NDI core in addition, it is reasonable to assume that in NDI$_2$-SnTPP:(OH)$_2$ the axis described by the two outer imide nitrogens is likely to intersect with the porphyrin metal centre. The centre-to-centre porphyrin-NDI separation, $R_{cc}$, was thus estimated utilising standard bond lengths as ca. 12.8 Å. Although no confirming crystallographic information was recorded, the magnitude of the inaccuracy has a limited impact on the values finally calculated. The values used previously for ZnTPP and NDI, hence $r_D = 5$ Å and $r_A = 3.5$ Å, were employed as the radii of the radical ions formed [21]. The results are shown in Table 6.1 and graphically in Figure 6.6. The calculated results strongly support the initial interpretation of the
6. An NDI\textsubscript{2}-SnTPP:(O\textsubscript{Ph}-BODIPY)\textsubscript{2} array

<table>
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<th>Toluene</th>
<th>PhCN</th>
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<td>(S_2)-excitation</td>
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<td>-1.01 (-0.71)</td>
</tr>
<tr>
<td>(S_1)-excitation</td>
<td>0.68 (0.08)</td>
<td>-0.20 (0.09)</td>
</tr>
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Table 6.1: Calculated free energy changes for photoinduced ET from SnTPP to an NDI moiety in NDI\textsubscript{2}–SnTPP:(OH)\textsubscript{2} chromophore triad in the solvents toluene and PhCN. Values calculated from (5.1) including the correction terms (5.1a) and (5.1b). Values in brackets calculated from (5.1), i.e. without consideration of the solvent environment.

ET is energetically feasible for porphyrin \(S_2\) excitation in both solvents, while the CS state energies are close to or above the \(S_1\) state and hence do not allow ET to proceed from the latter.

Figure 6.6: Energy level diagram showing calculated CS state energies for photoinduced ET from SnTPP(OH)\textsubscript{2} to an NDI moiety in the NDI\textsubscript{2}–SnTPP:(OH)\textsubscript{2} chromophore triad. \(S_0\), \(T_1\), \(S_1\) and \(S_2\) are the local porphyrin electronic states. \(CS\textsubscript{toluene}\) and \(CS\textsubscript{PhCN}\) are the CS state energy levels calculated from the Rehm-Weller equation (5.1) including the correction terms (5.1a) and (5.1b) [22]. The CS level is calculated from (5.1), i.e. without consideration of the solvent environment. Non-labelled arrows refer to ET processes between SnTPP and NDI.

ET from \(S_2\) has to occur on a time scale that is faster than the typical solvation of ion species. The solvent-dependent contribution to the calculated CS state energies are hence likely to exaggerate the relative changes compared to the CS state energies calculated from (5.1), which only assumes the here more appropriate framework of an intramolecular charge transfer [23]. The relative changes do however offer an
6.1. Results and discussion

explanation of the observed solvent dependency. The CS state in toluene is clearly above $S_1$ and CR accordingly repopulates the latter. In PhCN the CS state is energetically too close to $S_1$ and CR therefore returns to the ground state species and hence reduces the $S_1$ emission intensity observed following $S_2$ excitation. $S_1$ excitation is energetically insufficient to allow CS to compete with ISC to the $T_1$ state. It is noted that no excited CS state is inferred in the proposed decay pathway. To investigate this further, the TA spectra were recorded in both solvents following excitation to the porphyrin $S_2$ state. The results of these measurements are shown in Figure 6.7.

The recorded spectra clearly show the signatures of $S_1$ to $T_1$ interconversion via ISC overlapped with the Q band bleach, very similar to those recorded for SnTPP:(OH)$_2$ (cf. Figure 6.4). Moreover in addition a component with a rapid formation during the first few ps followed by a decay over the following 200 ps can be observed across the probed wavelength range, most distinctly at 580 nm. Given the close similarity between the ground and excited state absorption properties of SnTPP:(OH)$_2$ and ZnTPP, as well as between the broad and featureless spectral profile of this component and that reported for the ZnTPP radical cation [24], it appears consistent to assign it to the SnTPP radical cation absorption. Due to the extensive spectral overlap, the extent of CR to either $S_1$ or $S_0$ is difficult to quantify from these measurements. The reduced $T_1$ state absorption intensity in PhCN compared to toluene, most notable at 490 nm (cf. Figures 6.7a&b), supports the interpretation of the bypassing of $S_1$ following CS in the case of the former. Biexponential fitting of the 580 nm traces return values for the rate constants of CR in toluene and PhCN as $3.7 \times 10^{10}$s$^{-1}$ and $2.5 \times 10^{10}$s$^{-1}$ respectively. Given that CR frequently occurs in the inverted region of ET [25–29], and the CS state in the more polar PhCN is stabilised relative to the corresponding state in non-polar toluene, an accelerated rate of CR would be expected for the former if the product state was
6. An NDI$_2$-SnTPP:(OPh-BODIPY)$_2$ array

Figure 6.7: TA spectra of 100 µM NDI$_2$-SnTPP:(OH)$_2$ chromophore triad in toluene (a) and PhCN (b) recorded up to 900 ps after 415 nm excitation. Kinetic profiles at selected wavelengths in toluene (c)&(e) and PhCN (d)&(f).
the same in both cases (cf. 4.2.2 and 5.4.1). The observation of opposite relative magnitudes hence adds further support to the assumption of differing product states following CR. Due to the extensive spectral overlap, as well as coinciding with the time scale of direct IC from $S_2$ to $S_1$, direct determination of the rate of CS from the TA data was not possible. However, from the observed extent of quenching a value very similar to that of the rate constant for IC from $S_2$ to $S_1$ in SnTPP:(OH)$_2$ can be inferred, i.e. ca. $8 \times 10^{11}$s$^{-1}$.

It is plausible to assume that the electronic coupling between the donor and acceptor depends on the dihedral angles between their respective planes and the plane of the phenyl linker. Greater planarity with at least one NDI branch in this array would allow for increased conjugation and hence increased orbital overlap and electronic coupling. The sterically favoured perpendicular arrangement [19, 30, 31] would however interrupt the equally energetically favourable conjugation and hence orbital overlap and electronic coupling [32, 33]. Obviously a dynamic distribution of conformations will be present in solution. The small yet discernible red-shift of the steady-state absorption spectra (cf. Figures 6.3a&b) suggests accordingly only a minor interaction between the NDI and the porphyrin moieties. ET from the porphyrin $S_2$ state occurs on the time scale that is fast relative to molecular motion. The fate of the porphyrin $S_2$-excited array to undergo either IC or ET might therefore depend on the specific conformation directly prior to excitation.

Returning to the overall NDI$_2$-SnTPP:(OPh-BODIPY)$_2$ array, these results suggest that SnTPP can function as an electron donor to NDI, but only if sufficient initial excitation energy is provided.
6. An NDI_{2}-SnTPP:(OPh-BODIPY)_2 array

6.1.3 Phenolate ligated SnTPP arrays

The systems discussed here are SnTPP:(OPh)_2 and SnTPP:(OPh-BODIPY)_2, which as mentioned above were investigated previously by Lazarides et al. [12], as well as the overall NDI_{2}-SnTPP:(OPh-BODIPY)_2 array, which differs from the former through the additional NDI moieties. As mentioned above, Lazarides et al. showed that in the systems investigated during their study, the SnTPP S_1 state is strongly quenched by ET from the phenolate, forming the porphyrin radical anion. In the case of the BODIPY-appended system, excitation of this moiety leads to EnT and population of the porphyrin S_1 state, which then decays by the ET process described. The steady-state emission spectra of these three arrays show no discernible porphyrin S_2 fluorescence (cf. Figures 6.3c&d), and the rates for CS reported by Lazarides et al. are similar to the SnTPP:(OH)_2 S_2 lifetime. It was therefore investigated whether excitation of the porphyrin S_2 state in these arrays results in decay pathways other than IC to S_1.

SnTPP:(OPh)_2

The TA spectra of this array following 415 nm excitation recorded in toluene and PhCN are shown in Figures 6.8a and 6.9a respectively. They are very similar in both employed solvents. They show a fast decay during the first few ps observable in the region around 500 nm and above 650 nm. This is matched by a corresponding rise most discernible at 570 nm, which is followed by a secondary decay over tens of ps returning to the baseline. All this is overlapped with the characteristic Q band bleach. Ascribing the 570 nm trace to the formation and subsequent decay of the SnTPP radical anion formed by ET from the phenolate is fully consistent with the corresponding report by Lazarides et al. as well as the inference of this process from fluorescence studies carried out previously [13, 14].

Excitation at 415 nm initially populates the porphyrin S_2 state. Whether the
6.1. Results and discussion

(a) SnTPP:(OPh)\(_2\) in toluene

(b) Kinetic profiles of SnTPP:(OPh)\(_2\) in toluene

(c) SnTPP:(OPh-BODIPY)\(_2\) in toluene

(d) Kinetic profiles of SnTPP:(OPh-BODIPY)\(_2\) in toluene

(e) NDI\(_2\)-SnTPP:(OPh-BODIPY)\(_2\) in toluene

(f) Kinetic profiles of NDI\(_2\)-SnTPP:(OPh-BODIPY)\(_2\) in toluene

Figure 6.8: TA spectra and kinetic profiles at selected wavelengths of 100 µM of (a)&(b) SnTPP:(OPh)\(_2\), (c)&(d) SnTPP:(OPh-BODIPY)\(_2\) and (e)&(f) NDI\(_2\)-SnTPP:(OPh-BODIPY)\(_2\) in toluene and recorded up to 100 ps after 415 nm excitation.
Figure 6.9: TA spectra and kinetic profiles at selected wavelengths of 100 µM of (a)&(b) SnTPP:(OPh)₂, (c)&(d) SnTPP:(OPh-BODIPY)₂ and (e)&(f) NDI₂-SnTPP:(OPh-BODIPY)₂ in PhCN and recorded up to 100 ps after 415 nm excitation.
rate of IC to $S_1$ in this array is similar to SnTPP:(OH)$_2$ is unclear, as the spectral overlap and the rapid CS occur on a similar time scale. The traces at 650 nm (cf. Figures 6.8b and 6.9b) show considerably slower decays than the corresponding traces for SnTPP:(OH)$_2$ (cf. Figures 6.4c&d). Employing the developed hybrid GTA method (cf. 2.5.4) and only including rates for CS from the porphyrin $S_2$ state and subsequent CR to the ground state in the kinetic model was insufficient to fit the data fully. Additionally including a rate for IC to $S_1$ fixed at the value determined for SnTPP:(OH)$_2$ and assuming the identical value for CS from the phenolate to both the $S_2$- and $S_1$-excited porphyrin allowed the data to be fitted completely. It is however inevitable that a greater number of variable parameters improves the fit quality. It is therefore only tentatively concluded that ET from the phenolate occurs in parallel to at least some initial IC to the porphyrin $S_1$ state. Based on the above assumptions the rate constants for ET to either the $S_2$- or $S_1$-excited porphyrin from the phenolate were derived as $ca. 5 \times 10^{11} \text{s}^{-1}$. The rate constant for CR was derived as $ca. 5.5 \times 10^{10} \text{s}^{-1}$. Both are in agreement with the values reported by Lazarides et al. [12].

ET to SnTPP during the $S_2$ state lifetime has been reported by Jang et al. [34]. They reported this for SnTPP axially ligated by two ferrocene-carboxyl units. They also stated that the SnTPP radical anion absorption is similarly featureless like that of the ZnTPP radical cation.

**SnTPP:(OPh-BODIPY)$_2$**

The TA spectra of this array shown in Figures 6.8c and 6.9c are very similar to those of SnTPP:(OPh)$_2$. The main differences are a moderate decrease in the overall transient decay rates, as well as the clearly discernible BODIPY bleach contribution centred around 500 nm [7, 9, 12, 35].
With respect to the porphyrin and BODIPY extinction coefficients at the excitation wavelength of 415 nm, partial excitation of the latter can be expected. The initial (inverted) rise of this bleach component within the time frame of the IRF is most certainly due to this competitive absorption leading to direct BODIPY excitation. There is however a further increase of this bleach, occurring over several ps, which cannot be explained by an overlapping absorption decay in this spectral region. IC of BODIPY from its higher excited states occurs on the considerably faster time scale of 100 to 230 fs [35, 36] and cannot explain such an increase in this bleach component. Further, a bleach contribution is unaffected by any excited state interconversion that does not repopulate the ground state.

The question therefore arises how the BODIPY ground state can be further depleted beyond the duration of the excitation pulse. Its reduction potential is $-1.2 \text{ V vs. SCE}$ [12]. The driving force for ET from the porphyrin is hence considerably reduced by ca. 0.6 eV compared to an NDI acceptor (cf. 6.1.2). It is therefore unlikely to be sufficiently energetically favourable to compete with other processes depleting the porphyrin $S_2$ state. In addition, orbital overlap between the porphyrin and BODIPY is limited by the phenolate linker. ET is therefore highly unlikely to be the cause of the additional BODIPY ground state depletion.

The alternative explanation would be EnT from the porphyrin $S_2$ state to the BODIPY $S_1$ state. As mentioned above, the reverse process populating the porphyrin $S_1$ state is highly efficient in this array. Lazarides et al. showed a close agreement between the observed rates of EnT and those calculated by Förster theory. It was stated that although this cannot be excluded, Dexter-type EnT is unlikely to occur in this array.

To further evaluate this possibility the Förster critical radius, $R_c$, for EnT from
the porphyrin $S_2$ state to the BODIPY $S_1$ state was calculated from the following standard equation [37–39]:

$$R_c = 0.2108 \left( \eta^4 \Phi_f \kappa^2 J(\lambda) \right)^{\frac{1}{6}} \quad (6.1)$$

where $\eta$ is the refractive index of the medium, $\Phi_f$ is the isolated donor’s fluorescence quantum yield, $\kappa^2$ is the dipole-dipole interaction orientation factor and $J(\lambda)$ is the Förster spectral overlap integral. The value employed for the donor’s fluorescence quantum yield was that reported for SnTPP:(Cl)$_2$, hence $\Phi_f = 8.4 \times 10^{-4}$ [15]. Based on the assumption of the dynamically averaged orientation of the donor and acceptor transition dipoles, $\kappa^2$ was set to $2/3$. The value of the Förster critical radius was thus calculated as 10.7 Å, which given the crystallographic derived SnTPP-BODIPY separation of $r_{DA} = 10.1$ Å [12] would imply an EnT efficiency of ca. 60%. The corresponding rate for Förster resonance EnT, $k_{FRET}$, was calculated from [38–40]:

$$k_{FRET} = \frac{1}{\tau_0} \left( \frac{R_c}{r_{DA}} \right)^6 \quad (6.2)$$

where $\tau_0$ is the donor excited state lifetime, which was taken from SnTPP:(OH)$_2$ as 1.3 ps. The value thus calculated for the rate constant of Förster resonance EnT was $1.1 \times 10^{12}$ s$^{-1}$. This value suggests that EnT would be sufficiently fast to at least partially compete with the other porphyrin $S_2$ deactivation pathways in this array.

The fitting of such a decay scheme, in which the final CS state can be formed directly from ET to the porphyrin $S_2$, to $S_1$ following IC from $S_2$ as well as EnT to BODIPY and back to $S_1$, was attempted using the hybrid GTA method. However, the spectral overlap, the very similar time scales and the number of employed fitting parameters do not permit a robust determination of the individual rate constants. From basic fits to the BODIPY bleach in the traces at 500 nm, which are
hampered by the obvious partial direct excitation contribution, the rate constant for Förster-type EnT from the porphyrin $S_2$ state is estimated as $ca. 2 \times 10^{11}s^{-1}$, which — given the assumptions stated above — is in reasonable agreement with the calculated value.

The derived value for the rate constant of this EnT is of a very similar magnitude to the rate constant for $S_2$-$S_1$ IC observed in SnTPP:(OH)$_2$ as well as the ET quenching by the phenolate. The spectral similarities between the various porphyrin species prohibit the accurate determination of their relative contributions to the porphyrin $S_2$ state decay. It can however be concluded that partial deactivation of the $S_2$ state excitation via EnT to BODIPY delays ET from the phenolate until the reverse EnT step re-excites the subsequently reduced porphyrin.

**NDI$_2$-SnTPP:(OPh-BODIPY)$_2$**

Finally, with reference to the complete array, the question remained whether, given the several avenues of porphyrin $S_2$ state deactivation, the ET process observed in NDI$_2$-SnTPP:(OH)$_2$ (cf. 6.1.2) can still occur. Combining EnT and ET is one of the goals artificial photosynthetic approaches try to achieve, in order to mimic more closely the function of the natural system. Table 6.2 lists the rate constants for the expected $S_2$ state deactivation derived from the various model compounds. Given the spectral similarities between the various expected intermediate and product species, distinguishing between the pathways is difficult. It assumes at the same time that the rate constants derived in one model system transfer without change to another. As discussed this is difficult to confirm, and even small changes would considerably affect the distribution amongst the various decay channels.

The question additionally arises as to how the NDI moieties interact with the SnTPP radical anion, possibly formed via ET from the phenolate. Similar to the
6.1. Results and discussion

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<td>SnTPP:(OPh-BODIPY)$_2$</td>
<td>$2 \times 10^{11}$</td>
<td>0.09</td>
</tr>
</tbody>
</table>

Table 6.2: Possible porphyrin $S_2$ state deactivation pathways in the NDI$_2$-SnTPP:(OPh-BODIPY)$_2$ array.

arguments for partial orbital overlap between SnTPP and NDI creating sufficient electronic coupling to allow ET to occur in the NDI$_2$-SnTPP:(OH)$_2$ array, the same extension of conjugation would allow stabilisation of the porphyrin radical anion. This would slow CR to the ground state. Beyond this, any SnTPP radical cation would be quenched by ET from the phenolate.

The TA spectra for this array following 415 nm excitation recorded in toluene and PhCN are shown in Figures 6.8e and 6.9e. Although there are minor relative intensity changes compared to the corresponding SnTPP:(OPh-BODIPY)$_2$ spectra, the overall spectral profiles and kinetics are very similar. This includes the kinetic profile of the BODIPY bleach component at 500 nm and therefore suggests that the same EnT process originating from the porphyrin $S_2$ state does occur in this array.

The comparison of these spectra does not allow any conclusions to be drawn in regard to whether direct ET from the porphyrin $S_2$ state to NDI can occur to at least some extent in this array. It can however be noted that in the TA spectra of the complete array a relatively slowly decaying and broadly absorbing feature persists in a higher relative amplitude compared to the non-NDI-substituted array spectra. From the overlapping Q band bleach signature a porphyrin-based species can be inferred as its predominant contributor. While both the decay rate and absorption profile of this component are similar to the SnTPP radical cation formed.
in the NDI$_2$-SnTPP:(OH)$_2$ array undergoing CR with the NDI radical anion, it is unlikely that the cation would not be quenched rapidly by the phenolate moiety. This component is therefore likely to be the SnTPP radical anion, which undergoes a slower CR with the phenolate cation, due to its partial delocalisation to the NDI periphery. Apart from this moderation of the rate of CR, the NDI-substitution does not appear to cause any significant deviations from the photophysical behaviour of the SnTPP:(OPh-BODIPY)$_2$ parent compound.

6.2 Conclusion

Given the number of photo- as well as redox-active components in the arrays investigated here, as well as the number of the in many cases parallel decay pathways, a definitive conclusion regarding the exact deactivation process following porphyrin S$_2$-excitation is difficult to draw. However, several points can be confirmed. SnTPP is actually capable of acting as a donor for photoinduced ET, albeit not from its S$_1$ state in this case, and as only moderately efficient from its S$_2$ state. This investigation also further confirms previous work demonstrating an ET interaction between SnTPP and the phenolate linker, which was presumably intended as the linking rather than a redox active component. If this process is undesirable, an alternative chromophore linkage has to be employed, especially given the rapid rate of quenching. While reports of EnT from photoexcited BODIPY to porphyrins are relatively numerous, the possibility of the reverse direction involving the porphyrin S$_2$ rather than S$_1$ state has previously not been investigated. Given the subsequent repopulation of the porphyrin S$_1$ state, this process provides no use for artificial photosynthetic constructs unless an alternative decay pathway following BODIPY excitation is provided.
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Conclusion

The overall goal of the work presented in this thesis was to investigate the photoinduced ET behaviour in several porphyrin-based RC mimics. A better understanding of these processes allows conclusions for the rational design of such constructs to be derived, and will aid the successful construction of artificial photosynthetic systems. The focus was on the differing assembly motifs and especially on the porphyrin $S_2$ state and its decay pathways in these systems.

As these ET processes occur on the ultrafast time scale, the standard spectroscopic techniques had to be extended to have the appropriate time resolution. To this end a time-resolved TA instrument employing a high RR amplified laser system was designed and constructed. While the techniques employed in this instrument are not conceptually new, it is nonetheless the first described implementation of a multichannel broadband detection using such a laser source. Compared to low RR arrangements its advantage is the lowered probe pulse energy, which greatly minimises coherent artefacts while maintaining a similarly high S/N. The shorter pulse-to-pulse separation is a very minor disadvantage. For the purpose of the TA data analysis a hybrid between GTA and MCR-ALS was developed. This allowed fitting data with overlapping negative signal contributions, typically the porphyrin ground state bleach, with any sequential as well as branched decay scheme model. One of the benefits of this method is the straightforward meaning of the calculated fit parameters.
The first investigation was into the decay pathways following excitation of the porphyrin $S_2$ state in loosely bound complexes of ZnTPP and $C_{60}$ in solution. While EnT could not be fully excluded, the TA measurements indicate that CS on a sub-ps time scale is responsible for the observed steady-state $S_2$ fluorescence quenching. This is one of the very few reported direct spectroscopic observations of such a CS state transient and the first for a non-covalent porphyrin-based system. The only partial $S_1$ state population upon CR suggests the CS state is in a vibrationally or electronically excited form that affects subsequent decay pathways. The direct application as a RC mimic is limited by the loose binding. However, the close donor-acceptor contact is very similar to many bulk organic photovoltaic devices, and the involvement of higher excited states in their behaviour and properties hence warrants further consideration.

The next system investigated was a ZnTPP-ANDI dyad, where the porphyrin is bound by a very short covalent link to the NDI's core-substituent. In this system photoinduced ET from the porphyrin $S_2$ state to a non-thermalised CS state is followed by CR to $S_1$, which in turn undergoes further CS. If wasteful CR to $S_1$ was to be avoided, a secondary, tightly coupled acceptor would be required. Core-substituted NDIs might here be promising candidates. Such an approach might allow preserving energy otherwise lost in thermal relaxation. The system studied displays relatively high donor-acceptor electronic coupling, which promotes ultrafast ET and suppresses long CS state lifetimes.

The next investigation focused on the suitability of several NDI derivatives as building blocks for the assembly of supramolecular RC mimics with ZnTPP. While the quinoline derivative does not appear to form complexes with ZnTPP, the pyridine and isoquinoline derivatives do so. The latter represents a previously not yet employed extension to the synthetic and structural tools that can be used in the
construction of supramolecular RC mimics. In the ZnTPP complexes with either pyrNDI or isoquinNDI, efficient ET from the porphyrin $S_1$ state forms a CS state that undergoes CR to the ground state over hundreds of ps. Long-lived CS states observed in such systems in polar solvents are shown to be likely due to ET from the $T_1$ state of uncomplexed porphyrin following diffusional encounter with an NDI acceptor. The solvent polarity dependence of the CS and CR rates in these complexes, as well as in the ZnTPP-ANDI dyad, confirm the frequent reports of CS occurring in the normal, and CR occurring in the inverted, region of ET. In the ZnTPP:isoquinNDI complexes an ET pathway starting from the porphyrin $S_2$ state and followed by a subsequent CR to $S_1$ is inferred. This is tentatively attributed to the involvement of the coordinating isoquinoline moiety’s frontier orbitals. It demonstrates that linking motifs can show behaviour extending beyond their intended structural role.

Finally, the larger NDI$_2$–SnTPP:(OPh-BODIPY)$_2$ array and several related model systems were investigated. In the covalent NDI$_2$–SnTPP:(OH)$_2$ triad, SnTPP can act as an ET donor, though not from $S_1$ and only moderately efficiently from $S_2$. In the arrays with phenolate moieties bound to the porphyrin metal centre, the excited states of the latter are rapidly quenched by ET from this ligand. While EnT from BODIPY to porphyrins is well-known, the reverse process originating from the latter’s $S_2$ state has not so far been investigated. Such EnT is inferred from the initial increase in the depletion of the BODIPY ground state following porphyrin $S_2$-excitation, although the subsequent EnT repopulating the $S_1$ state limits practical applicability. In the overall array the NDI moieties appear to slow the decay of the CS state formed between a phenolate ligand and SnTPP to a small degree. This is attributed to the increased stabilisation of the latter’s radical anion charge by partial delocalisation onto the NDI groups.
Conclusion

To summarise, the photoinduced ET behaviour of several porphyrin-based RC mimics has been elucidated, and the involvement of the porphyrin $S_2$ state in the ET and EnT behaviour of several of these systems demonstrated. Incorporating the outcomes into the design of RC mimics, possibly with the inclusion of a secondary acceptor, might allow minimising the losses that occur during the transfer of the incident photon’s energy to usable redox potential. Covalent linkage is evidently not necessary, although a small donor-acceptor separation and hence increased electron coupling is likely to be a requirement. However, a small separation at the same time increases the competing CR rates. The likely extension of the acceptor frontier orbitals onto the linking moieties in both the ZnTPP-ANDI and the ZnTPP:isoquinNDI dyads, and the similar porphyrin $S_2$ state ET behaviour observed in both, together suggest that this might be transferable to novel systems.

In recent years considerable advances have been achieved in the understanding and construction of artificial photosynthetic systems. However, there remain considerable challenges in the synthesis of constructs that can meet the design and cost criteria for useful systems that can contribute to sustainable energy solutions for mankind.
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